Chapter 4
Equivalence of First and Second Laws

4.1 Laws of Thermodynamics: Local and Global Forms

Building on Carnot's foundation for the determination of motive power in steam engines, Clausius introduced two functions of state and built around them the first and second law of thermodynamics. Perhaps due to his desire to formulate a "mechanical theory of heat," he constructed the first law as a generalization of the conservation of energy in mechanics, resulting in the definition of the internal energy, and allowed for violations in the definition of the entropy as a function of state to be the indicators of the irreversibility of what Clausius termed "uncompensated transformations." In this chapter, we will show that Clausius's choice is, to a large extent, a matter of taste: The entropy function can be preserved, and violations in the internal energy can determine the "ordering of states" when less than maximum work is performed by the engine.

We can say that Carnot knew the second law, but was ignorant of the first law. This is why he had to introduce his general and special axioms in order to determine the work done. In contrast, Clausius knew the first law, but allowed for violations in the second law to accommodate the possibility of wasted heat given off to the cold reservoir. Whereas both formulations attribute an increase in heat rejected to the cold reservoir as the origin of irreversibility, or the wasted portion of work that the engine was capable of doing, they do so in different ways. By reformulating Carnot's general and special axioms, it will be possible to obtain an analytical expression for this wasted heat, whereas Clausius can only derive an inequality for his "uncompensated" transformations.

We begin by formulating the local the first and second laws in terms of exterior calculus that we introduced in Sect. 3.1. The "natural" state plane is the temperature, volume, T, V-plane, as Carnot was the first to realize. The state vector, $\mathrm{d}r$, has therefore the components $(\mathrm{d}T, \mathrm{d}V)$. Fundamental to all of thermodynamics is the calorimetric equation of state which expresses the heat, Q^1, a 1-form, in terms of the heat covector, $\mathcal{H}$, with components (C_v, L_v), where C_v and L_v are the heat capacity at constant volume and the latent heat, respectively. Consequently, the calorimetric

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equation of state, or what we have referred to as the doctrine of latent and specific heats, can be written as

$$Q^1 = \mathcal{H} \cdot \mathrm{d}r = C_v \mathrm{d}T + L_v \mathrm{d}V. \tag{4.1}$$

Recall the first law that introduces the notion of a work covector, $\mathcal{F}$, with components $(0, p)$, where p is the pressure. The work done by the system, W^1, also a 1-form, is given by

$$W^1 = \mathcal{F} \cdot \mathrm{d}r = p \cdot \mathrm{d}V. \tag{4.2}$$

With the aid of the heat and work covectors, the first and second laws can be formulated as

$$\nabla \wedge \mathcal{H} = \nabla \wedge \mathcal{F} \tag{4.3}$$

and

$$\begin{aligned} \nabla \wedge \mathcal{H}/T = 0 \qquad &\text{or} \qquad \nabla \wedge V^s \mathcal{H} = 0, \\ \nabla \wedge \mathcal{H} = T\mathcal{H} \wedge \nabla T^{-1}, \qquad &\text{or} \\ \nabla \wedge \mathcal{H} = V^{-s} \mathcal{H} \wedge \nabla V^s. & \end{aligned} \tag{4.4}$$

In fact, the second law (4.4) just specifies the curl of the heat vector, and any term which when multiplied by T to form an adiabatic invariant will do just as well in any other state plane containing T as a coordinate axis. Eliminating the curl of the heat covector between (4.3) and (4.4) yields the Clausius–Clapeyron equation

$$\nabla \wedge \mathcal{F} = T\mathcal{H} \wedge \nabla T^{-1} \qquad \text{or} \qquad \nabla \wedge \mathcal{F} = V^{-s} \mathcal{F} \wedge V^s, \tag{4.5}$$

which Clausius needed, but not Carnot.

Clausius formulates the first law (4.3) so that Carnot's axiom would be deducible from it, and it would not appear as "independent principles in the theory of heat." In component form, (4.3) is

$$\frac{\partial p}{\partial T} = \frac{\partial L_v}{\partial T} - \frac{\partial C_v}{\partial V}, \tag{4.6}$$

which when multiplied by the element of area, $\mathrm{d}V\,\mathrm{d}T$, and integrated over the limits of temperature and volume of the engine express the work in terms of the circulation in the heat current

$$W = \iint_{\mathcal{A}} \frac{\partial p}{\partial T} \mathrm{d}V \mathrm{d}T = \oint_{\mathcal{C}} Q^1. \tag{4.7}$$

Recall that the path, $\mathcal{C}$ is transversed in the clockwise direction enclosing the area $\mathcal{A}$ according to Green's theorem (2.33).

The second laws (4.4) are given in component form as

$$\nabla \wedge \mathcal{H} = \frac{L_v}{T} = \frac{sC_v}{V}. \tag{4.8}$$

It would appear that the second equality, unlike the first, depends on the specific nature of the working substance. This is contrary to Carnot's axiom that the work done by the engine should be independent of the working substance. However, since $sC_v = R$, the universal gas constant, the second inequality does not, indeed, violate Carnot's axiom. Integrating (4.8) over a cycle gives

$$\oint_{\mathcal{C}} Q^1 = \iint_{\mathcal{A}} \frac{L_v}{T} \mathrm{d}V \mathrm{d}T = \iint_{\mathcal{A}} \frac{sC_v}{V} \mathrm{d}V \mathrm{d}T. \tag{4.9}$$

Whereas Clausius formulates the first law so as to deduce Carnot's axioms, we will modify Carnot's axioms to define a nonmaximal work function, which is bounded above by Carnot's expression. This saves the second law and allows the energy balance equation to account for irreversibility.

4.2 Carnot's Modified Axiom and His Criterion for Irreversibility

Carnot [1824] states his general axiom in the following way:

> The motive power of heat is independent of the working substances that are used to develop it. The quantity is determined exclusively by the temperatures of the bodies between which, at the end of the process, the passage of caloric has taken place.

Carnot's special axiom says

> The amount of work done by the engine is a product of the heat and a function of the two temperatures only.

Carnot does not specify whether the heat is that which is absorbed at the hot reservoir, Q_{h}, or that rejected to the cold reservoir, Q_{c}, since, according to caloric theory, the two are one and the same. Truesdell (1980) is correct in saying that Carnot's general and special axioms are equivalent for engines working between infinitesimal temperature differences, but they fail to be equivalent when the temperature differences are finite. We will use this lack of equivalency for finite temperature differences to our advantage so as to transform the global expressions for the second laws into inequalities that comply with Carnot's special axiom. In modified form, Carnot's axiom can be stated as:

> The amount of motive power (work) is a product of the heat given off to the cold reservoir and either: (i) a function of the extreme temperatures which cannot depend upon their absolute values, or (ii) a function of the extreme values in the volume, which, again, cannot depend on their absolute values but only on their ratios.

The former condition is necessary in order that the work does not increase without bound when the high temperature, or maximum volume, is allowed to increase without limit. The latter conditions require the variables to appear only in a ratio.

Consequently, Carnot's modified special axiom can be formulated as:

$$W = F(x/y)Q_c. \tag{4.10}$$

The function $F(x/y)$ obeys the functional equation

$$F(x/y) = F(x) - F(y), \tag{4.11}$$

where if $x = y$, $F(1) = 0$, so that a fall in temperature, or increase in volume, is necessary in order to produce motive power. If $x = 0$ (or $y = 0$), $F(0) = 0$ would be the only solution. The solution to the functional equation is $F(x) = \ln x$ for all values of $x \neq 0$. The logarithm saves the universality of Carnot's modified axiom, for, otherwise, the adiabatic exponent, s, of the volume would appear independently of the heat capacity, C_v. Since both depend upon the specific nature of the working substance, they would violate Carnot's axiom. In other words, *the heat released to the cold reservoir does not depend upon the details of the cycle, or the working substance, once the extreme temperatures, or volumes, are fixed*. If the temperature is chosen, the natural cycle is Carnot's, while if the volume is chosen, the Otto cycle appears as the natural one.

4.2.1 Carnot Cycle

The well-known Carnot cycle, shown in Fig. 4.1 consists of four branches:

1. $1 \to 2$: An isothermal absorption of heat Q_h at the high temperature, T_h.
2. $2 \to 3$: An adiabatic expansion which reduces the temperature from T_h to T_c.

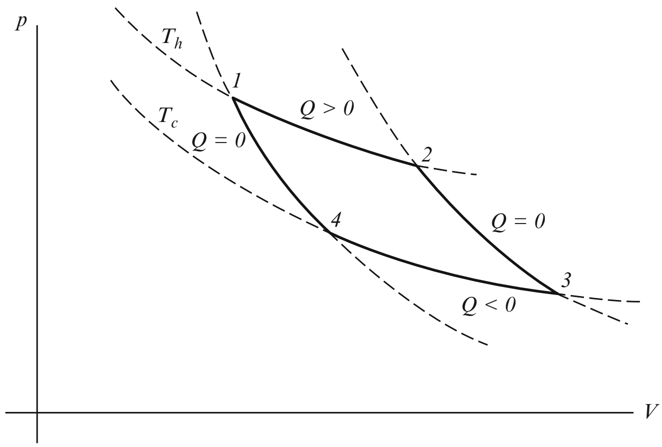


Fig. 4.1 Carnot cycle

3. 3 → 4: An isothermal compression in which heat Q_c is given up to the cold reservoir at temperature, T_c.
4. 4 → 1: An adiabatic compression which increases the temperature from T_c to T_h and returns the engine to its initial state.

Since the maximum work depends on the difference in heats absorbed at the boiler and given up at the condenser, Carnot's special axiom leads to an expression of the actual work given by the inequality

$$\oint_C Q^1 = \int_{V_4}^{V_3} \int_{T_\mathrm{c}}^{T_\mathrm{h}} \frac{L_v}{T} \mathrm{d}V \mathrm{d}T \geq \int_{V_4}^{V_3} L_v \mathrm{d}V \cdot \int_{T_\mathrm{c}}^{T_\mathrm{h}} \frac{\mathrm{d}T}{T}. \tag{4.12}$$

The inequality expresses a loss of work when the heat given off to the cold reservoir is split off in the area integral leaving an integral which is only a function of the two temperatures. Clausius also uses the heat rejected to the cold reservoir to calculate the work in his original formulation (Magie 1899).

Since the volume dependence of L_v does not enter into the discussion, we need to only assume that the latent heat has a power temperature dependence, T^n, for any $n \geq 1$, which includes the ideal gas as a lower limit. Thus,

$$\int_{T_\mathrm{c}}^{T_\mathrm{h}} T^{n-1} \mathrm{d}T \geq T_c^n \int_{T_\mathrm{c}}^{T_\mathrm{h}} \frac{\mathrm{d}T}{T},$$

and this explains why the heat rejected to the cold reservoir must be used in calculating the nonmaximal work done by the engine. Integrating we get the well-known inequality (Hardy 1952)

$$\ln x \leq m\left(x^{1/m} - 1\right), \quad x > 0, \tag{4.13}$$

for any positive m.

Inequality (4.13) is very easily proven by a general method that determines the extremum of a function (Hardy 1952), which, in this case is $\phi(x) = \ln x - x + 1$. This function has a maximum at $x = 1$, where it vanishes. Consequently, $\phi(x) \leq 0$ for all values of $x > 0$.

It, therefore, follows that the nonmaximal work done by the engine is

$$W = Q_\mathrm{c} \ln \frac{T_\mathrm{h}}{T_\mathrm{c}}. \tag{4.14}$$

Using the reversible amount of heat given up to the cold reservoir,

$$Q_\mathrm{c} = T_\mathrm{c} Q_\mathrm{h} / T_\mathrm{h}, \tag{4.15}$$

(4.14) is seen to have the upper bound

$$W = Q_\mathrm{h}\frac{T_\mathrm{c}}{T_\mathrm{h}}\ln\left(\frac{T_\mathrm{h}}{T_\mathrm{c}}\right) \leq \left(1-\frac{T_\mathrm{c}}{T_\mathrm{h}}\right)Q_\mathrm{h}, \tag{4.16}$$

as a consequence of the inequality (4.13). This unambiguously shows that Carnot "knew the second law, without knowing the first" – contrary to what Truesdell (1980) claims.

The last term in (4.16) defines the Carnot efficiency

$$\eta_\mathrm{C} = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}}, \tag{4.17}$$

so that the middle term defines a nonmaximal efficiency

$$\eta = \frac{T_\mathrm{c}}{T_\mathrm{h}}\ln\left(\frac{T_\mathrm{h}}{T_\mathrm{c}}\right). \tag{4.18}$$

Table 4.1 compares Carnot, (4.17), the nonmaximal, (4.18), and the observed, efficiencies of three power plants. The nonmaximal efficiency comes much closer to the observed efficiency than the Carnot efficiency.

As a first approximation to the efficiency (4.18), we may take the arithmetic average of its upper and lower bounds,

$$\frac{T_\mathrm{h}-T_\mathrm{c}}{T_1} \leq \ln\frac{T_\mathrm{h}}{T_\mathrm{c}} \leq \frac{T_\mathrm{h}-T_\mathrm{c}}{T_\mathrm{c}}, \tag{4.19}$$

namely,

$$\ln\frac{T_\mathrm{h}}{T_\mathrm{c}} \approx \frac{T_\mathrm{h}^2-T_\mathrm{c}^2}{2T_\mathrm{h}T_\mathrm{c}}, \tag{4.20}$$

which becomes better the closer $T_\mathrm{c}/T_\mathrm{h}$ is to 1. The work that the engine does is approximately

$$W \approx \eta_\mathrm{approx}Q_\mathrm{h}, \tag{4.21}$$

where

$$\eta_\mathrm{approx} = \frac{1}{2}\left(1-\frac{T_\mathrm{c}^2}{T_\mathrm{h}^2}\right). \tag{4.22}$$

Table 4.1 Nonmaximal, Carnot, and observed efficiencies

Power source	T_2 (K)	T_G (K)	T_1 (K)	T_A (°C)	η (%)	η (Carnot) (%)	η (Obs) (%)
W Thurrock (Spalding 1966)	298.15	499.9	838.15	568.15	36.8	64	36
CANDU (Griffiths 1974)	298.15	413.38	573.15	162.5	34	48	30
Larderello (Chierice 1964)	353.15	429.82	523.15	165	26.5	32	16

The smaller the ratio, $x := T_c/T_h$, the greater the efficiency (4.18), which is a concave function of x, and, hence, is an object that is to be maximized. We may use the property of concavity to establish

> The greatest amount of work that can be done is the difference between the heat absorbed at the hot reservoirs and the heat rejected at the cold reservoirs, independent of whether the cycle is closed or not.

Denoting the heats absorbed at the hot reservoirs, $Q_{\mathrm{h}\,i}$, and the heats rejected at the cold reservoirs, $Q_{\mathrm{c}\,i}$, the work done over a cycle is

$$\begin{aligned} W &= \sum_i^n Q_{\mathrm{c}\,i} \ln \frac{Q_{\mathrm{h}\,i}}{Q_{\mathrm{c}\,i}} \\ &\leq \sum_i^n Q_{\mathrm{c}\,i} \ln \Big(\sum_i^n Q_{\mathrm{h}\,i} \Big/ \sum_i^n Q_{\mathrm{c}\,i} \Big) \\ &\leq \sum_i^n Q_{\mathrm{h}\,i} - \sum_i^n Q_{\mathrm{c}\,i} = W_{\max}. \end{aligned} \tag{4.23}$$

The inequality in the second line of (4.23) is Jensen's for a concave function, while the inequality in the third line follows from inequality (4.13). According to Carnot, the internal energy will exist as a function of state only when the maximum amount of work is performed during the cycle. That is, the change in the internal energy will vanish, and it is for this reason we say that Carnot was ignorant of the first law.

In analogy with the first law – but without requiring the exactness of $\mathrm{d}E$ – we may construct the energy balance equation

$$W = \sum_i^n Q_{\mathrm{h}\,i} - \sum_i^n Q_{\mathrm{c}\,i} - \Delta E, \tag{4.24}$$

where

$$\Delta E \geq 0 \tag{4.25}$$

for all irreversible transitions. Consequently, if Clausius salvaged Carnot's theory by merely rejecting the conservation of heat, he could not have considered a general conservation of energy independent of the limitations set upon the engine. If state b is accessible from state a then

$$E_b - E_a > 0, \tag{4.26}$$

asserting that the only way a state can be reached is if work is expended in getting there.

All other mechanical processes which exchange work and energy do not enter into Carnot's formulation of engine efficiency. Moreover, any adiabatic process that is not coupled to a pair of isothermal, isochoric, or isobaric ones would violate

inequality (4.26). In other words, there can be no work done by any thermodynamic system that does not operate between two different temperatures, two different volumes, or two different pressures in a cycle.

If the heat absorbed at the hot reservoir were used to calculate the work, there would be no correspondence between W and $(Q_\mathrm{h} - Q_\mathrm{c})$, and the need for giving off heat to the cold reservoir. It was caloric theory that required the cold reservoir for heat conservation. When it was realized that heat could be converted into work by Joule, Mayer, and Holtzmann, it only diminished the quantity of heat given off to the cold reservoir – but did not obliterate its importance!

The accessibility of any state from a given one is limited by

$$\Delta E \leq W_{\max}. \tag{4.27}$$

From the balance of energy for nonmaximal work,

$$W = -Q_\mathrm{h} x \ln x = (1-x)Q_\mathrm{h} - \Delta E, \tag{4.28}$$

it follows that

$$0 \leq \Delta E = \Big(1 - x + x\ln x\Big) Q_h \leq (1-x)^2 Q_h = \eta_C W_{\max}. \tag{4.29}$$

The first inequality follows from

$$1 - x \geq -x \ln x, \tag{4.30}$$

while the second inequality follows from (4.13). Inequality (4.29) establishes a limit of accessibility of a state from a given one in terms of the maximum work performed by the engine.

4.2.2 Otto Cycle

The Otto cycle, shown in Fig. 4.2, consists of four strokes:

1. $1 \to 2$: The gas in the cylinder is compressed adiabatically from $V_{\max}$ to $V_{\min}$.
2. $2 \to 3$: Combustion modelled as heat absorption at constant volume, $V_{\min}$.
3. $3 \to 4$: The hot gas expands adiabatically from $V_{\min}$ to $V_{\max}$.
4. $4 \to 1$: The pressure valve opens and temperature drops, modelled as heat rejection at constant volume, $V_{\max}$.

The second law is given by the second equality in (4.8) integrated over the limits in the T, V-plane

$$\oint_C Q^1 = \int_{T_2}^{T_3} \int_{V_{\min}}^{V_{\max}} \frac{sC_v}{V} \mathrm{d}V\,\mathrm{d}T. \tag{4.31}$$

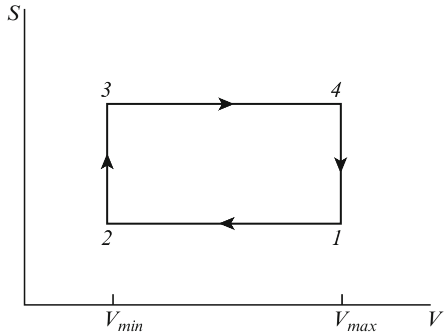


Fig. 4.2 Otto cycle

Now, the heat capacity is either a constant, as it is for an ideal gas, or a function of the adiabatic parameter, $z = TV^s$, as it is for a degenerate gas, so that (4.31) can be converted into the inequality

$$\oint_C Q^1 = \int_{T_2}^{T_3} C_v \mathrm{d}T \int_{V_{\min}}^{V_{\max}} s\frac{\mathrm{d}V}{V} \geq \int_{T_1}^{T_4} C_v \mathrm{d}T \cdot \ln\left(\frac{V_{\max}}{V_{\min}}\right)^s. \tag{4.32}$$

The first term on the right-hand side of (4.32) is the heat absorbed at constant volume, Q_h, which models the combustion process. In order that work be done, this must be greater than the heat given off at constant volume, Q_c. This is expressed by the inequality in (4.32).

Consider the gas to be ideal, $C_v = \text{const}$. The adiabatic conditions

$$V_{\min}^s T_3 = V_{\max}^s T_4 \qquad \text{and} \qquad V_{\min}^s T_2 = V_{\max}^s T_1 \tag{4.33}$$

give the ratio of the temperatures as $T_3/T_2 = T_4/T_1$, and hence, with the aid of inequality (4.13), we get the work done by the piston, according to Carnot's modified special axiom, over a cycle as

$$\begin{aligned} W &= C_v(T_4 - T_1)\ln\left(\frac{V_{\max}}{V_{\min}}\right)^s \\ &\leq C_v\frac{(T_4 - T_1)}{V_{\min}^s}\left(V_{\max}^s - V_{\min}^s\right) \\ &= \eta_O Q_h = W_{\max}, \end{aligned} \tag{4.34}$$

where $Q_h = C_v(T_3 - T_2)$, and the efficiency of the Otto cycle is

$$\eta_O = \frac{W_{\max}}{Q_h} = 1 - \left(\frac{V_{\min}}{V_{\max}}\right)^s = 1 - \frac{T_1}{T_2}. \tag{4.35}$$

The ratio, $V_{\max}/V_{\min}$, is known as the compression ratio (Cravalho 1981) for the engine.

This should be compared with the usual method of calculating the maximum work (Cravalho 1981). The heat absorbed as the engine goes from stage 2 to 3 is $Q_{\mathrm{h}} = C_v(T_3 - T_2)$. The heat rejected on going from 4 to 1 is $Q_{\mathrm{c}} = C_v(T_4 - T_1)$. Hence, the maximum amount of work that the Otto engine can perform is

$$\begin{aligned} W_{\max} &= Q_{\mathrm{h}} - Q_{\mathrm{c}} \\ &= C_v\Big(T_3 - T_2\Big)\Big(1 - \frac{T_1}{T_2}\Big) \\ &= C_v\Big(T_3 - T_2\Big)\left[1 - \Big(\frac{V_{\min}}{V_{\max}}\Big)^s\right], \end{aligned} \tag{4.36}$$

which is precisely (4.34).

The Otto engine is comparable to Carnot's cycle. Using the adiabatic relations between the temperatures, and $sC_v = R$, the work given in (4.34) can be made to read

$$W = \Big(\frac{V_{\min}}{V_{\max}}\Big)^s \eta_{\mathrm{C}} Q_{\mathrm{h}}, \tag{4.37}$$

where the Carnot efficiency is given by

$$\eta_{\mathrm{C}} = 1 - \frac{T_2}{T_3} = 1 - \frac{T_1}{T_4}, \tag{4.38}$$

and the heat absorbed in the isothermal expansion at the temperature of the hot reservoir, T_3, is

$$Q_{\mathrm{h}} = RT_3 \ln\Big(\frac{V_{\max}}{V_{\min}}\Big). \tag{4.39}$$

4.2.3 Brayton Engine

The Brayton engine consists of two adiabats coupled by two isobaric curves, as shown in Fig. 4.3.

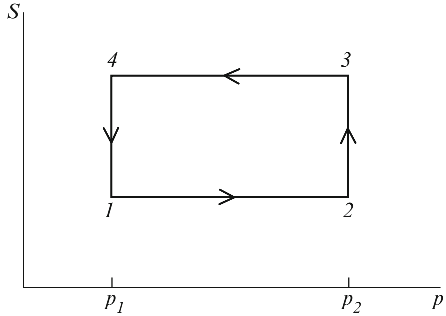
The four strokes are:

1. $1 \to 2$: Adiabatic compression of fuel and air
2. $2 \to 3$: Heating by fuel combustion at constant pressure
3. $3 \to 4$: Expansion of the gas
4. $4 \to 1$: Rejection of the gas to the atmosphere

The 1-form of the heat will be given in terms of temperature and pressure as independent variables,

$$Q^1 = C_p\,\mathrm{d}T + L_p\,\mathrm{d}p, \tag{4.40}$$

Fig. 4.3 Brayton cycle



where C_p is the heat capacity at constant pressure and $L_p < 0$ is the latent heat with respect to the pressure. The integrating denominator for (4.40) is $p^{s/(s+1)}$, and this gives a heat current

$$\int_C Q' = \int_{p_{\min}}^{p_{\max}} \int_{T_2}^{T_3} \frac{s}{s+1} \frac{C_p}{p} \mathrm{d}p\mathrm{d}T. \tag{4.41}$$

Again, we see that this is a universal expression since $sC_p/(s+1) = R$.

We can convert (4.41) into an inequality by replacing the heat absorbed in step $2 \rightarrow 3$ by the heat rejected in step $4 \rightarrow 1$

$$\int_C Q' \geq \int_{T_1}^{T_4} C_p \mathrm{d}T \cdot \ln \left(\frac{p_{\max}}{p_{\min}}\right)^{s/(s+1)}. \tag{4.42}$$

Specializing to an ideal gas with constant heat capacity, the work done over a Brayton cycle is

$$W = C_p(T_4 - T_1) \ln \left(\frac{p_{\max}}{p_{\min}}\right)^{s/(s+1)}. \tag{4.43}$$

Using the fundamental inequality (4.13) and the adiabatic conditions

$$\left(\frac{p_{\max}}{p_{\min}}\right)^{s/(s+1)} = \frac{T_1}{T_2} = \frac{T_4}{T_3} \tag{4.44}$$

gives the maximum work $W_{\max} = \eta_{\mathrm{B}} Q_{\mathrm{h}}$, where the efficiency,

$$\eta_{\mathrm{B}} = 1 - \left(\frac{p_{\max}}{p_{\min}}\right)^{s/(s+1)}, \tag{4.45}$$

is given in terms of the pressure ratio (Cravalho 1981), and the heat produced by fuel combustion is

$$Q_{\mathrm{h}} = C_p(T_3 - T_2). \tag{4.46}$$

Here, again, the roles have been inverted compared to Carnot's cycle: The heat produced, (4.46), is given in terms of the ideal gas rather than the logarithm of the ratio of volumes, while the efficiency, (4.45), is expressed in terms of the pressure ratio, rather than the ratio of volumes under isothermal expansion.

4.2.4 Endoreversible Engine

With the scope of determining real efficiencies that are realized in actual power plants, Curzon and Ahlborn (1975) published a highly influential paper that was eventually to become a new branch of thermodynamics called "finite-time thermodynamics." What they did was to replace the isothermal expansion and compression steps in Carnot's cycle by heat fluxes that are created by differences in temperatures between the working fluid and the temperatures of the boiler and condenser.

The internal engine operated in a completely reversible fashion, and all irreversibilities were relegated to the coupling of the engine to the reservoirs. Such an engine has been called "endoreversible" (Rubin 1979).

The Curzon – Ahlborn engine in Fig. 4.4 distinguishes between the temperatures of the reservoirs and the temperatures of the working fluid at which heat is absorbed and rejected. The temperature of the boiler is T_1 and a quantity of heat Q_1 is absorbed at the fluid temperature, $T_{1\mathrm{w}} < T_1$, where the subscript w stands for "warm." However, we already know that according to Carnot's argument, the heat engine will absorb a quantity of heat that is inferior to Q_1. Likewise, the temperature of the working fluid, when it comes in contact with the condenser, is $T_{2\mathrm{w}}$, which is higher than the temperature T_2 of the condenser.

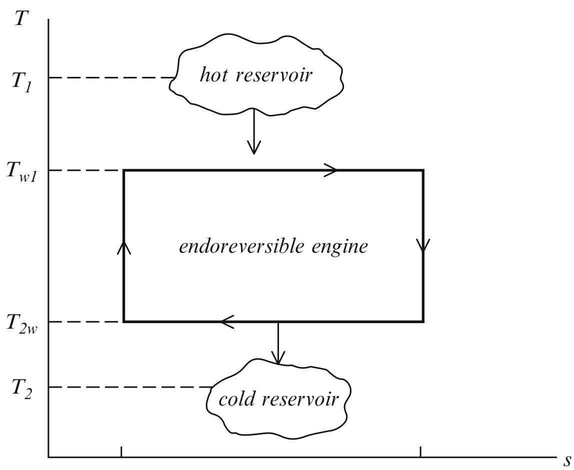


Fig. 4.4 Endoreversible engine

The cycle, shown in Fig. 4.4, consists of four steps:

1. The working fluid at the high temperature T_1 is cooled to a temperature, $T_{1\mathrm{w}}$, at a constant minimum volume, V_{min}.
2. By an adiabatic expansion, it is further cooled to the lowest temperature T_2 where it reaches a maximum volume, V_{max}.
3. The working fluid is heated isochorically to an intermediate temperature, $T_{2\mathrm{w}}$.
4. It is finally compressed adiabatically to reach the initial, high temperature, T_1.

The simplest assumption for the kinetics of the heat transfer is that the heat transfer rate $\dot{Q}_1$ is proportional to the temperature difference $(T_1 - T_{1\mathrm{w}})$ between the hot reservoir and the working fluid, viz.,

$$\dot{Q}_1 = \alpha(T_1 - T_{1\mathrm{w}}), \tag{4.47}$$

where α is the product of the area of the vessel and the thermal conductance (the inverse of the thermal resistance) per unit area of surface perpendicular to the direction of heat transfer. α has units of kilowatts per degree Kelvin. Because steam engines involve the bulk flow of matter under steady flow conditions, we prefer, to make it more compatible with what follows, to use the capacity rate $\dot{m}c_v$ (Cravalho 1981a) as the coefficient of proportionality. This is to say that if the fluid can be modelled as an ideal gas, the change in energy due to heat transfer rate is a linear function of the temperature difference in the heat exchanger. The units of the capacity rate are the same as α.

Curzon and Ahlborn associate the duration of the isothermal expansion, t_1, with the time of the flow, and multiply both sides of (4.47) by this time interval to obtain the total heat transfer

$$Q_1 = \alpha t_1(T_1 - T_{1\mathrm{w}}) = m_1 c_v(T_1 - T_{1\mathrm{w}}), \tag{4.48}$$

where m_1 is the amount of mass transported in the time interval t_1. In the same way Curzon and Ahlborn assume a temperature difference between the working fluid and the cold reservoir to create an outward heat flux

$$-Q_2 = \beta t_2(T_2 - T_{2\mathrm{w}}) = m_2 c_v(T_2 - T_{2\mathrm{w}}). \tag{4.49}$$

Again, the heat rejected is assumed to be proportional to the difference in temperature between the working fluid and the temperature of the lower reservoir. We have set βt_2 equal to the heat capacity, $m_2 c_v$, where m_2 is the product of the mass flow rate, $\dot{m}_2$, and its duration t_2. We know only their product, not how small or large the flow rate is or how large or small the time interval t_2 is. Only their product is relevant, and $m_2 c_v$ is determined by the ratio of the heat transferred, $-Q_2$, to the difference in temperature $(T_2 - T_{2\mathrm{w}})$. An adiabatic compression brings the working fluid back to its original state.

The crucial step in the Curzon–Ahlborn analysis is their condition for reversibility

$$\frac{Q_1}{T_{1\mathrm{w}}} = \frac{Q_2}{T_{2\mathrm{w}}}. \tag{4.50}$$

Maximizing the power,

$$P = \frac{Q_1 - Q_2}{t_1 + t_2}, \tag{4.51}$$

with respect to the unknown intermediate temperatures, yields an efficiency,

$$\eta = 1 - \sqrt{\left(\frac{T_2}{T_1}\right)}, \tag{4.52}$$

which is less than the Carnot efficiency, (2.32). Their condition for maximum power (Curzon 1975, Eq. 9) is the first equality in

$$\frac{T_{2\mathrm{w}} - T_2}{T_1 - T_{1\mathrm{w}}} = \sqrt{\left(\frac{\alpha T_2}{\beta T_1}\right)} = \frac{\alpha t_1}{\beta t_2}\frac{T_{2\mathrm{w}}}{T_{1\mathrm{w}}} = \frac{\alpha t_1}{\beta t_2}\sqrt{\left(\frac{T_2}{T_1}\right)}. \tag{4.53}$$

The second equality uses Curzon and Ahlborn's condition for reversibility, (4.50), and the last equality expresses the ratio of the intermediate temperatures in terms of the reservoir temperatures. By equating the second and fourth terms in (4.53), Curzon and Ahlborn obtain the condition

$$\beta/\alpha = \dot{m}_2/\dot{m}_1 = (t_1/t_2)^2. \tag{4.54}$$

Furthermore, it has been claimed that the Curzon–Ahlborn engine has a net entropy gain (De Vos 1992)

$$\Delta S = (\eta_{\mathrm{C}} - \eta)\,\frac{Q_1}{T_2} > 0. \tag{4.55}$$

So how can there be a criterion of reversibility (4.50) at the same time there is an increase in the entropy? It is therefore not unreasonable to ask what is the meaning of (4.50).

From (4.54) there is a good reason to believe that something is amiss. We would have expected a relation such as

$$m_1 = \dot{m}_1 t_1 = \dot{m}_2 t_2 = m_2 = m, \tag{4.56}$$

expressing the conservation of mass instead of (4.54). If the latter condition is used to evaluate (4.50), we obtain

$$2T_{i\mathrm{w}} = T_i + \sqrt{(T_1 T_2)}, \quad (i = 1, 2) \tag{4.57}$$

so that the sum,

$$T_{1\mathrm{w}} + T_{2\mathrm{w}} = \frac{1}{2}(T_1 + T_2) + \sqrt{(T_1 T_2)},$$

is the sum of the arithmetic and geometric average temperatures. Introducing these values for the intermediate temperatures in (4.48) and (4.49) give

$$Q_1 = mc_v \frac{1}{2}\sqrt{T_1}\left(\sqrt{T_1} - \sqrt{T_2}\right), \tag{4.58a}$$

$$Q_2 = \frac{1}{2} mc_v \sqrt{T_2}\left(\sqrt{T_1} - \sqrt{T_2}\right), \tag{4.58b}$$

under the homogeneity condition (4.56). Their difference yields the maximum work output

$$\begin{aligned} W &= Q_1 - Q_2 \\ &= \frac{1}{2} mc_v (\sqrt{T_1} - \sqrt{T_2})^2 \\ &= mc_v\Big[\frac{1}{2}(T_1 + T_2) - \sqrt{(T_1 T_2)}\Big], \end{aligned} \tag{4.59}$$

found by Curzon and Ahlborn from maximizing the power (4.51) with respect to the intermediate temperatures $T_{1\mathrm{w}}$ and $T_{2\mathrm{w}}$ whose optimal values are given in (4.57).

The adiabatic conditions that relate the various temperatures to the extremum volumes are

$$T_1 V_{\mathrm{min}}^s = T_{2\mathrm{w}} V_{\mathrm{max}}^s \qquad \text{and} \qquad T_{1\mathrm{w}} V_{\mathrm{min}}^s = T_2 V_{\mathrm{max}}^s. \tag{4.60}$$

Since the work cannot be superior to the heat transfer

$$\oint_C Q^1 \geq \int_{T_2}^{T_{2\mathrm{w}}} \int_{V_{\mathrm{min}}}^{V_{\mathrm{max}}} \frac{sC_v}{V} \mathrm{d}V \mathrm{d}T = C_v\Big(T_{2\mathrm{w}} - T_2\Big) \ln\left(\frac{V_{\mathrm{max}}^s}{V_{\mathrm{min}}^s}\right). \tag{4.61}$$

Calling the right-hand side of (4.61) the work, its maximum value is

$$W_{\mathrm{max}}(T_{1w}) = Q_1\left(1 - \frac{T_2}{T_{1w}}\right) = C_v\Big(T_1 - T_{1w} - \frac{T_G^2}{T_{1w}} + T_2\Big), \tag{4.62}$$

which we take as a function of the unknown intermediate temperature, $T_{1\mathrm{w}}$. This temperature can be determined by requiring that the work, (4.62), be maximum (Leff 1987). The condition is

$$T_{1w}^* = T_G = \sqrt{(T_1 T_2)}, \tag{4.63}$$

which determines the optimal temperature of the engine as the geometric mean temperature.

We know from the principle of maximum work that this is the lowest final temperature possible when the elements of an unevenly heated body are connected to

perfect reversible engines which do maximum work (Thomson 1853a). The expression for the maximum work

$$W^*_{\max} = 2C_v(T_A - T_G) = \eta_{\max} Q^*_{1\,\max} \tag{4.64}$$

is guaranteed by the arithmetic–geometric mean inequality, where

$$\eta_{\max} = 1 - \sqrt{\left(\frac{T_2}{T_1}\right)} \tag{4.65}$$

is the Curzon–Alhborn efficiency, and the optimum heat flux into the system is

$$Q^*_{1\,\max} = C_v(T_1 - T_G). \tag{4.66}$$

We now inquire as to whether any work can be had from the heat rejected, and, in so doing, gain insights into the limitations of the second law. The work we want to consider is

$$W(T_{2w}) = Q_2\left(1 - \frac{T_{2w}}{T_1}\right) = C_v\left(T_{2w} - T_2 - \frac{T_{2w}^2}{T_1} + \frac{T_2 T_{2w}}{T_1}\right), \tag{4.67}$$

and maximize it with respect to the intermediary temperature, just as we did with (4.62). The necessary condition for an extremum is:

$$T^*_{2w} = \frac{1}{2}(T_1 + T_2) = T_A, \tag{4.68}$$

which results when perfect engines at different temperatures come into thermal contact and fail to perform any work. In order to perform work, the temperature must be lowered, which is possible by putting anew the system in thermal contact with the coldest of the surroundings objects at T_2. Introducing (4.68) into (4.67) gives the maximum work

$$W^* = \frac{C_v}{T_1}(T_A^2 - T_G^2) = \eta^* Q^*, \tag{4.69}$$

where the efficiency and heat absorbed are

$$\eta^* = 1 - \frac{T_A}{T_1} \tag{4.70}$$

and

$$Q^* = C_v(T_A - T_2), \tag{4.71}$$

respectively.

However, maximum work can always be expressed as a difference in heats, so (4.69) must be equivalent to:

$$W^* = Q_h - Q_c,$$

resulting in the reversibility condition:

$$\frac{Q_h}{T_A} = \frac{Q_c}{T_H} \tag{4.72}$$

So if the temperature of the hot reservoir is $T_h = T_A$, the temperature of the cold reservoir will be the harmonic mean temperature, $T_c = T_H = T_G^2/T_A$. Thus, in order to get work from a system that has already achieved a common temperature, T_A, without any work being performed, it has to placed anew in thermal contact with the coldest of its surroundings. This echoes Kelvin's original statement of the second law:

> It is impossible by means of an inanimate material agency to derive a mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

To this we may add:

> The mechanical effect of a perfect engine is always inferior to that which would result from releasing heat to the coldest of its surroundings.

For, otherwise, we would have $T_H = T_2$, and this would imply a vanishing temperature difference. Hence, we must always have $T_H > T_2$ if work is to be done by a fall in temperature. The efficiency and heat uptake are:

$$\eta^* = 1 - \frac{T_H}{T_A} \tag{4.73}$$

and

$$Q^* = C_v T_A, \tag{4.74}$$

respectively. The final temperature T_H, is a fraction, T_G/T_A, of the geometric mean temperature, T_G.

We can now determine the difference between the maximum and minimum work that the engine can perform. The greater the difference is the greater its capacity to do work. Letting $x = T_2/T_1$ we can write Carnot's expression for the work as

$$W = -Q_1 x \ln x = (1-x)Q_1 - \Delta E, \tag{4.75}$$

where the first term on the right-hand side is the Carnot expression for the absolute maximum work. In other words, the ratio of the change in energy to the heat absorbed,

$$\Delta E/Q_1 = [1 - x - x\ln(1/x)] = (\eta_C - \eta)\,, \tag{4.76}$$

equals the difference between the Carnot, or maximum, efficiency and nonmaximal efficiency (3.65) that we obtained by calculating the work by using the heat rejected to the cold reservoir.

The Flaw in the Endoreversible Engine

There is a fatal flaw in the preceding analysis and it lies with (4.50): It is not the condition that the process be reversible. According to Thomson (1852b), a process is perfectly reversible when

> ...the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermodynamic engine working with a source and refrigerator at the higher and lower of the temperatures respectively.

In symbols, Thomson claims that

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \tag{4.77}$$

is the true condition for the cycle to be reversible, which is *not* the Curzon–Ahlborn criterion of reversibility (4.50). We have already discussed how Thomson arrived at (4.77).

Instead of (4.50), we should assume that an engine absorbs a quantity of heat Q_1 at temperature T_1 and emits the quantity of heat $(T_M/T_1)Q_1$ at any temperature $T_M < T_1$, viz.,

$$Q_2 = \frac{T_M}{T_1} Q_1. \tag{4.78}$$

Because there is a complete symmetry between the upper and lower reservoirs, we can equally well write

$$Q_1 = \frac{T_M}{T_2} Q_2, \tag{4.79}$$

but, now, with the proviso $T_M > T_2$. Equating the ratio of heats absorbed and rejected in (4.78) and (4.79) give the correct final temperature, $T_M = T_G = \sqrt{(T_1 T_2)}$, and introducing the Curzon–Ahlborn criterion for reversibility (4.50) give

$$\frac{T_{1\mathrm{w}}}{T_{2\mathrm{w}}} = \frac{T_1}{T_G} = \frac{T_G}{T_2}. \tag{4.80}$$

This fixes the ratio of the intermediary temperatures.

The differences between their values and those of the two reservoirs is determined by introducing (4.57) into (4.48) and (4.49). We then obtain

$$Q_1 = mc_v (T_1 - T_{1\mathrm{w}}) = \frac{1}{2} mc_v (T_1 - T_G), \tag{4.81}$$

$$Q_2 = mc_v (T_{2\mathrm{w}} - T_2) = \frac{1}{2} mc_v (T_G - T_2). \tag{4.82}$$

The difference between the two quantities of heat, (4.81) and (4.82), is the maximum work (4.59). The work is always positive definite unless the two temperatures are equal; the inequality is a consequence of the arithmetic–geometric mean inequality.

Several corrections to Tait's *Sketch* (1868, pp. 101–102), which he attributes to Thomson's (1853) paper, should be noted. Tait considers an element of mass dm of

an "irregularly heated body," whose temperature is t and has specific heat c. Denoting T as the temperature to which "the whole body can be brought by means of perfect engines, so that all the heat lost is converted into work." In the first equation on p. 101, Tait gives the adiabatic equilibration as

$$0 = \int \mathrm{d}m \int_T^t c\, \mathrm{d}t \frac{T}{t}.$$

However, there should be no capital T in the integrand. As Tait correctly observes, this equation gives us a means of determining the final temperature T and anticipates the Cashwell–Everett paper by a hundred years! Tait then goes on to determine the work as

$$W = J \int \mathrm{d}m \int_T^t c \frac{t-T}{t} \mathrm{d}t = J \int \mathrm{d}m \int_T^t c\, \mathrm{d}t,$$

which he claims follows from the preceding equation. However, the integrand should just be c and not $c(t-T)/t$. Here, he is confusing the work done $J(Q-Q_0)$ with $JQ(t-t_0)/t$, where Q_0 is the heat given out at the lower temperature t_0.

An Isothermal Endoreversible Engine

The heat conduction mechanism that Curzon–Ahlborn used for absorbing heat at the furnace and rejecting a smaller quantity at the refrigerator can be replaced by other mechanisms of heat absorption and rejection. Since the Curzon–Ahlborn engine absorbs heat by creating a difference in temperature between the boiler and the working fluid and rejects heat by a temperature difference between the working fluid and the condenser, it would, in Carnot's opinion, absorb less heat than if the working fluid were at the same temperatures of the reservoirs of which they are in contact. We can replace this mechanism by a moving boundary which expands when in contact with the boiler and compresses when in contact with the condenser, at constant temperature, just as in the original Carnot cycle.

However, both the internal energy and entropy are extensive quantities and are linear in the volume, and hence the first and second laws are incomparable (Lavenda 2005). In other words, no inequality results from means of the same order. The metrical entropy is additive, being a first-order homogeneous function, while all that is required of the "empirical" entropy is that it has the same value for all states that are accessible to it by quasistatic adiabatic transitions (Buchdahl 1966). What is required is another adiabatic potential that is not a first-order homogeneous function in order to allow us to compare means of different orders, and thereby establish the maximum property.

Unlike the empirical entropy, the change in the metrical entropy, in a quasistatic transition of a composite system, is the sum of the changes of the entropies of the subsystems making up the composite system. For the ideal gas, the metrical entropy, S, is related to the empirical entropy z logarithmically

$$S(z) = mR \ln z^{1/s}, \tag{4.83}$$

where R is the gas constant. The second law,

$$T\,dS(z) = TS'(z)\,\mathrm{d}z = \frac{mRT}{s\,z}\,\mathrm{d}z = \frac{mR\,dz}{sV^s} = \mathrm{d}Q, \tag{4.84}$$

shows that V^s is also an integrating factor (Einbinder 1948; Lavenda 2005) for the heat [cf. p. 42],

$$\frac{mR}{s}\mathrm{d}z = V^s\mathrm{d}Q = \sum_i^n V^s(L_{vi}\,\mathrm{d}V + C_{vi}\,\mathrm{d}T). \tag{4.85}$$

We make two simplifications: equal masses and assume the gas to be ideal, in which case $L_{vi} = p$, for each i, which is Holtzmann's (1848) conjecture, the latter ensuring that the internal energy will be a function of the temperature alone. Then, adiabatic equilibration for an isothermal expansion,

$$\Delta z = sT\sum_i^n \int_{V_i}^{V_M} v^{s-1}\mathrm{d}v = T\Big(nV_M^s - \sum_i^n V_i^s\Big) = 0, \tag{4.86}$$

identifies the mean of order s,

$$V_{M_s} = \Big(\frac{1}{n}\sum_i^n V_i^s\Big)^{1/s}, \tag{4.87}$$

as the final volume of the composite system.

The maximum heat absorbed in this isothermal expansion is

$$Q = mRT\sum_i^n \int_{V_i}^{V_{M_s}} \frac{\mathrm{d}v}{v} = nmRT\,\ln\Big(\frac{V_{M_s}}{V_G}\Big) > 0, \tag{4.88}$$

where

$$V_G = \Big(\prod_{i=1}^n V_i\Big)^{1/n} \tag{4.89}$$

is the geometric mean volume, $G = M_0$. Inequality (4.88) follows again from the fact that means are monotonically increasing functions of their order and $s > 0$. If n cells, initially at finite volumes $V_1, V_2, \ldots, V_n$ were brought into mechanical contact, and left alone for an indefinite amount of time, the final, common, volume would be given by the geometric mean (4.89).

Comparison of Endoreversible Engines

In this paragraph, we compare the isochoric engine of Curzon–Ahlborn and the isothermal engine. The efficiency of the isothermal engine is

$$\eta = 1 - \Big(\frac{V_G}{V_{M_s}}\Big)^s. \tag{4.90}$$

The maximum work output

$$W = \eta Q_1 = \frac{n}{s} mRT_1 \Big(1 - \frac{V_G^s}{V_{M_s}^s}\Big) \ln\Big(\frac{V_{M_s}^s}{V_G^s}\Big) \tag{4.91}$$

is the product of (4.90) and (4.88).

In order to compare the two engines, we set $n = 2$ and use the adiabatic constraints $\sigma_1 = V_1^s T_1 = \text{const.}$ and $\sigma_2 = V_2^s T_2 = \text{const.}$ These adiabats convert the mean of order s for the volume, (4.87), into the inverse of the harmonic mean, $H = M_{-1}$, for the temperature

$$V_{M_s}^s = \frac{1}{2}(V_1^s + V_2^s) = \frac{1}{2}\Big(\frac{1}{T_1} + \frac{1}{T_2}\Big) = \frac{1}{T_H} = \frac{T_A}{T_G^2}, \tag{4.92}$$

and the geometric mean of the volume, (4.89), into the inverse of the geometric mean of the temperature,

$$V_G^s = \sqrt{\big(V_1^s V_2^s\big)} = \frac{1}{\sqrt{(T_1 T_2)}} = \frac{1}{T_G}. \tag{4.93}$$

Because we will be concerned only with their ratio, we have dispensed with the arbitrary constants in (4.92) and (4.93). Equation (4.93) highlights the very important point that the same adiabatic conditions that hold for the volume and temperature individually also hold for their means.

The efficiency (4.90) can be expressed in terms of the ratio of the two mean temperatures as

$$\eta = 1 - \frac{T_G}{T_A}, \tag{4.94}$$

which is always positive thanks to the geometric–arithmetic inequality. The maximum heat uptake,

$$Q_1 = \frac{2}{s} mRT_{M_\infty} \ln\Big(\frac{T_A}{T_G}\Big), \tag{4.95}$$

can be approximated for small differences between the arithmetic, T_A, and geometric, T_G, means by

$$Q_1 \simeq \frac{2}{s} mRT_{M_\infty} \frac{(T_A - T_G)}{T_G}, \tag{4.96}$$

where $T_{M_\infty} = T_1$ denotes the highest attainable temperature. Therefore, the approximate expression for the maximum work is

$$W \simeq \frac{2}{s} mR \frac{T_{M_\infty}}{T_A} \frac{(T_A - T_G)^2}{T_G}. \tag{4.97}$$

Table 4.2 Expression for the efficiencies of the Carnot, Curzon-Ahlborn, and isothermal engines

engine	η
Carnot	$\dfrac{T_1 - T_2}{T_1}$
Curzon–Ahlborn	$1 - \sqrt{(T_1 T_2)}/T_1$
Isothermal	$1 - \sqrt{(T_1 T_2)}/\frac{1}{2}(T_1 + T_2)$

The last factor has the form of Karl Pearson's $\chi^2 = (T_A - T_G)^2/T_G$, which is a measure of the deviation from the expected value, T_G. In other words, χ^2 is expressed in terms of the "observed" frequencies, T_A, and the "expected" frequencies, T_G (Cramér 1946).

For comparison purposes, we express the efficiency (4.52), heat uptake, (4.58a), and the work output, (4.59) of the Curzon–Ahlborn engine in terms of mean values,

$$\eta = 1 - \frac{T_G}{T_{M\infty}}, \tag{4.98}$$

$$Q = mc_v T_{M\infty} \frac{T_A - T_G}{T_1 - T_G}, \tag{4.99}$$

and

$$W = mc_v(T_A - T_G), \tag{4.100}$$

respectively. The efficiencies are shown in Table 4.2.

For the West Thurrock coal fired steam plant (Spalding 1966), which has an efficiency of 36%, the Carnot efficiency is 64% and the Curzon–Ahlborn and isothermal efficiencies are 40% and 12%, respectively. This result is not surprising because the latter uses the average temperature of the two reservoirs as the higher temperature, as can be seen from (4.94), and the Curzon–Ahlborn engine uses the temperature of the hottest reservoir, which is apparent from (4.98). The former is clearly a very inefficient engine. The efficiencies are listed in Table 4.2.

For an ideal gas, $mc_v = R/s$, the heat uptakes of the two engines are roughly the same for the same power plant, and the work output of the isothermal engine is only 40% that of the Curzon–Ahlborn engine.

4.2.5 Stefan–Boltzmann Law from the Carnot Cycle

In 1884 Boltzmann used a Carnot cycle to establish theoretically the empirical law found by Stefan for the dependency of the energy of thermal radiation upon the absolute temperature. Boltzmann envisioned a cylinder and piston containing thermal radiation. The piston moves without friction and both the walls of the cylinder as well as the piston are impervious to the flow of heat. There is an outlet at the side opposite to the piston, O, in Fig. 4.5, where heat can enter and leave.

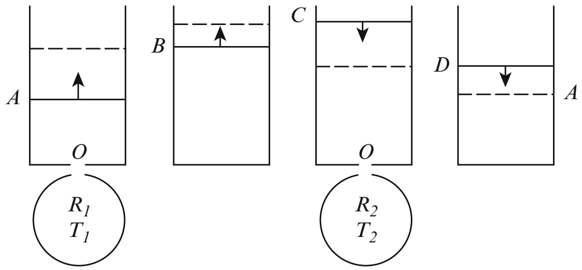


Fig. 4.5 The Carnot cycle according to Stefan and Boltzmann

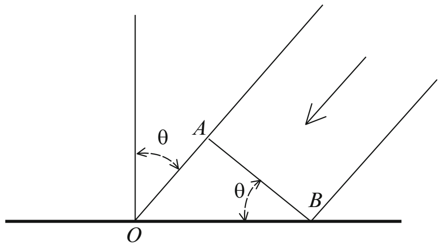


Fig. 4.6 Radiation falling obliquely on a surface

Initially the piston is in contact with an isothermal reservoir at temperature T_1. If the outlet is opened, radiation will flow into the cylinder until there is the same energy density ε_1 in the cylinder as in the isothermal enclosure. To determine the pressure due to isotropic radiation, we consider radiation falling perpendicularly on a surface. If ε is the energy density of the incoming waves, they will carry with them ε/c units of momentum per unit volume. Thus, to each unit of area in unit time there will be $c\varepsilon$ units of energy per unit time and a momentum ε per unit area per unit time. The pressure felt by the absorbing or reflecting surface is, therefore, ε, since both pressure and energy density have the same dimensions.

Now, if the radiation falls obliquely, at an angle θ with respect to the normal, the energy that crosses a unit area normal to the rays (AB in Fig. 4.6) has an area increased by an amount $1/\cos\theta$ than if they were falling normally on the surface (OB in Fig. 4.6). Moreover, the momentum suffers a decrease by an amount $\cos\theta$ than if the rays were normal to the surface. Consequently, the radiation pressure is

$$p = \varepsilon \cos^2\theta.$$

This radiation pressure must be averaged over an element of solid angle about the origin, O, $2\pi \sin\theta \mathrm{d}\theta$, and, then to determine its mean value, this must be divided by half of the whole solid angle about O, which is 2π. In this way, we find the average radiation pressure as

$$\bar{p} = \varepsilon \int_0^{\pi/2} \cos^2\theta \sin\theta \,\mathrm{d}\theta = \frac{1}{3}\varepsilon. \tag{4.101}$$

However, Boltzmann did not arrive at (4.101) in this way. Rather, he reasoned that the energy density should be divided equally among the walls of the container, each wall receiving a pressure of $\varepsilon/3$. To see why his reasoning was fallacious, he needed just to consider an ideal gas in which $p = \frac{2}{3}\varepsilon$; that is, twice as large as the radiation pressure he was using. Surely, Boltzmann knew the result he was after!

We may now consider the following cycle:

1. The piston starts at the initial position A in Fig. 4.7 with an initial volume V_1 and pressure $\bar{p}_1$. The piston moves upward slowly until it reaches B, so as to heed Lazare Carnot's warning that in order to determine maximum performance there should be no sudden changes or impacts, i.e., the process should be quasistatic. In order to maintain the radiation energy density constant, energy must be added through the opening, O, which places it in contact with reservoir R_1 at temperature T_1. Just how much energy enters is governed by the following two considerations:

   - Work is being done on the piston by pulling it up. If the temperature remains at T_1, ε_1, and likewise $\bar{p}_1$, will remain constant. Hence, the work will be

   $$W_1 = \frac{1}{3}\bar{p}_1 (V_2 - V_1) \,. \tag{4.102}$$

   - The interior volume of the cylinder has increased by an amount $(V_2 - V_1)$, requiring an additional energy of $\varepsilon_1(V_2 - V_1)$. Hence, the heat content that is added by radiation is

   $$H_1 = \frac{4}{3}\varepsilon_1(V_2 - V_1). \tag{4.103}$$

   This is represented by the horizontal line AB in Fig. 4.7.

   Note that the isotherms are horizontal lines instead of being curves sloping downward as in the case of a perfect gas. However, this is still a perfect gas, but a perfect gas of a different kind, i.e., a radiation gas, and not a material gas that conserves particle number. The heat content added during the isothermal expansion is H_1, the enthalpy which must come from the external reservoir R_1 in order to keep the working fluid at temperature T_1.

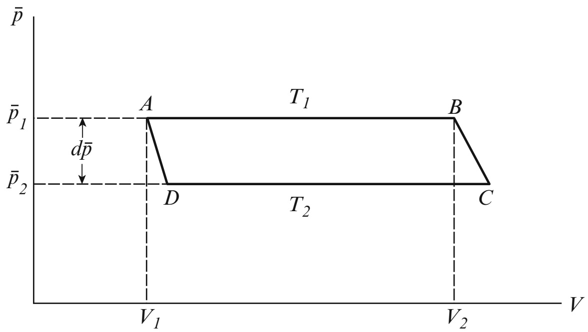


Fig. 4.7 A Carnot cycle in the $\bar{p}V$-plane whose working substance is radiation

2. Upon arrival at B, the outlet O is covered by a perfectly reflecting tap thereby isolating the interior of the cylinder from the outside world. A further expansion to C is carried out. Without energy from the outside this work consumes energy from within: The energy density decreases from ε_1 to ε_2, which is accompanied by a drop in temperature to T_2. Obviously, the pressure also decreases by a proportional amount. This adiabatic expansion is shown by the straight line BC in Fig. 4.7.

   If the expansion is a small one, we may replace the temperature difference, $(T_1 - T_2)$, by its infinitesimal, $\mathrm{d}T$. This being the case, the change in the energy density $(\varepsilon_1 - \varepsilon_2)$ may be replaced by $\mathrm{d}\varepsilon$, and since (4.101) holds, we get

$$\mathrm{d}\bar{p} = \frac{1}{3}\mathrm{d}\varepsilon, \tag{4.104}$$

   which is the change in the radiation pressure due to adiabatic expansion.
3. The working substance is now placed in contact with the isothermal reservoir R_2, which is at temperature T_2. The tap on the outlet is removed, in the third diagram in Fig. 4.5, and the piston is pushed downward until it reaches state D in Fig. 4.7. The compression serves to increase the density of radiation within the cylinder and since it must remain in equilibrium with the isothermal reservoir R_2, radiation must pass from the cylinder to the reservoir. But, because the compression is done so slowly the energy density is kept at ε_2, for any change in the energy density would necessitate a corresponding change in the temperature. The heat content which leaves the engine is H_2, analogous to that which it absorbed at the higher temperature T_1.
4. Having reached D, which is determined by the ratio of the volumes – the only free parameter available – the radiation undergoes further compression which brings it back to its initial state A.

The net effect has been to perform a closed cycle $ABCD$. If the pressure change is small, the total work is approximately the area of the rectangle $(V_2 - V_1)\mathrm{d}\bar{p}$. Although this is not exactly true, because we are neglecting the two small triangles at the ends, it will be true asymptotically, viz., in the limit as $\mathrm{d}\bar{p} \to 0$. The work accomplished by our engine will be

$$\mathrm{d}W = (V_2 - V_1)\,\mathrm{d}\bar{p} = \frac{1}{3}\,(V_2 - V_1)\,\mathrm{d}\varepsilon. \tag{4.105}$$

The efficiency of the Carnot engine is defined as usual

$$\eta_{\mathrm{C}} = \frac{\mathrm{d}W}{H_1} = \frac{T_1 - T_2}{T_1} = \frac{\mathrm{d}T}{T}.$$

Inserting the value for the work, (4.105), and the expression for the heat content, (4.103), lead to

$$\frac{\frac{1}{3}\mathrm{d}\varepsilon}{\frac{4}{3}\varepsilon_1} = \frac{\mathrm{d}T}{T_1}.$$

The subscripts are now superfluous and can be dropped since it must hold for all values of the energy density and temperature. The resulting ordinary differential equation

$$\frac{d\varepsilon}{\varepsilon} = 4\frac{dT}{T}$$

can be immediately integrated to give the well-known T^4 or, Stefan's law

$$\varepsilon = aT^4,$$

where a is a constant of integration.

The emissive power of a blackbody, $\mathcal{E}$, consisting of thermal radiation, is related to the energy density, ε by $\varepsilon = 4\mathcal{E}/c$. Since the latter varies as T^4 so does the former, and we can write

$$\mathcal{E} = \sigma T^4,$$

with another constant of proportionality, σ, known as the Stefan–Boltzmann constant, and fixes the constant of integration $a = 4\sigma/c$.

4.2.6 Relativistic Carnot cycle

In his first volume of *Die Relativitätstheorie*, von Laue (1919) proposes a Carnot cycle between a stationary system and one in relative motion to it. Because the proper temperature will be lower than the stationary temperature, relative motion will cause a temperature difference together with the possibility of performing work. It is rather odd that 15 years later, Tolman (1934) in his *Relativity, Thermodynamics, and Cosmology* was to reproduce von Laue's cycle without even the slightest mention of who the discoverer really was!

Due to the invariance of the pressure in special relativity, the cycle had to be contemplated as occurring under isobaric conditions. The relativistic Carnot cycle will occur in four steps:

1. $A \to B$ Isobaric and isothermal expansion with heat uptake Q_1 at T_1
2. $B \to C$ Reversible adiabatic acceleration to the velocity u
3. $C \to D$ Reversible and isothermal compression with heat rejection Q_2 at T_2
4. $D \to A$ Reversible adiabatic deceleration which restores the system the original state

von Laue (as well as Tolman) worked with mechanical quantities thereby making the analysis much more complicated than necessary. It suffices to consider only internal changes with thermodynamic quantities.

The heat uptake in the first step is

$$Q_1 = H_B - H_A = (m_B - m_A)\, c^2, \tag{4.106}$$

where $H_i = E_i + pV_i$ is the thermodynamic enthalpy of state i, and we have used the equivalence of heat and mass (Lavenda 2002) in establishing the second equality. According to Planck (1907), not only the energy density contributes to the inertial mass, but, in addition, there are stresses that are acting on the surface, and if these stresses are normal to the surface, the mass density will be

$$\varrho = \frac{\varepsilon + p}{c^2},$$

with a corresponding momentum given by

$$\frac{(\varepsilon + p)u}{c^2}.$$

Likewise, the heat released to the condenser is

$$Q_2 = H_C - H_D = (m_C - m_D)\, c^2, \tag{4.107}$$

which is reckoned positive. From the fact that the enthalpy decreases in a state of motion,

$$m_C = \gamma^{-1} m_B \qquad \text{and} \qquad m_D = \gamma^{-1} m_A, \tag{4.108}$$

where $\gamma = 1/\sqrt{(1 - u^2/c^2)}$ is the Lorentz factor, we may write the heat rejected, (4.107), in terms of the heat uptake as

$$Q_2 = \gamma^{-1} (m_B - m_A)\, c^2 = \gamma^{-1} Q_1. \tag{4.109}$$

The work then will be the difference of (4.106) and (4.109), viz.,

$$\begin{aligned} W &= Q_1 - Q_2 = (m_A - m_B)\, c^2 \left(1 - \gamma^{-1}\right) \\ &= Q_1 \left(1 - \gamma^{-1}\right) = Q_2 \,(\gamma - 1)\,. \end{aligned} \tag{4.110}$$

From Carnot's principle, we may deduce from the first equality in the second line of (4.110) that

$$T_2 = \gamma^{-1} T_1. \tag{4.111}$$

This says that a system in relatively uniform motion will have a temperature lower than that of the system in a state at rest. A comparison of (4.109) and (4.111), gives the condition of reversibility as:

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}.$$

From (4.111) it follows that the Carnot efficiency is

$$\eta_{\mathrm{C}} = 1 - \gamma^{-1}, \tag{4.112}$$

which approaches unity as $u \to c$, since $T_2 \to 0$. And from the second line of (4.110) we may deduce that the motion is hyperbolic, with uniform acceleration in the second and fourth steps, as we shall now show.

In a uniformly accelerating frame in one dimension, the definition of hyperbolic (additive) time τ is

$$\tau/\tau_0 = \ln\left(\frac{t + x/c}{t - x/c}\right) = \ln K = \frac{1}{2}\ln\left(\frac{1+\beta}{1-\beta}\right), \tag{4.113}$$

where the scale is set by $\tau_0 = c/g$, and g is the acceleration constant of gravity at the surface of the earth. The second and last equalities testify to the fact that the motion is not uniform, i.e., $u = x/t$, but, rather

$$u = \frac{2x/t}{1 + (x/ct)^2}. \tag{4.114}$$

This is the relative speed of two systems with equal and opposite velocities. Although known as the Einstein composition law for velocities, (4.114) was discovered by Poincaré.

Taking the derivative of both sides of (4.113) with respect to t results in

$$\frac{g}{c}\frac{d\tau}{dt} = \frac{1}{1-\beta^2}\frac{d\beta}{dt} \tag{4.115}$$

in a state of uniform acceleration. A moving clock will appear to go more slowly than one at rest (time dilatation), so that the proper time τ will be related to the coordinate time t by

$$\frac{d\tau}{dt} = \gamma^{-1}. \tag{4.116}$$

Introducing (4.116) into (4.115) results in

$$g/c = \frac{1}{(1-\beta^2)^{3/2}}\frac{d\beta}{dt} = \frac{d}{dt}\frac{\beta}{\sqrt{1-\beta^2}}. \tag{4.117}$$

In a state of uniform acceleration, the Lorentz transform

$$x' = x\cosh\alpha - ct\sinh\alpha, \tag{4.118a}$$

$$t' = t\cosh\alpha - (x/c)\sinh\alpha \tag{4.118b}$$

rotates the coordinate and time through an “imaginary” angle, α. Introducing the “rapidity” (Robb 1911), according to its definition $\beta = \tanh\alpha$, which relates the

Euclidean measure of the relative velocity, β, to its hyperbolic measure α,[1] we find $\cosh\alpha = 1/\sqrt{(1-\beta^2)}$, and $\sinh\alpha = \beta/\sqrt{(1-\beta^2)}$. We can thus write the Lorentz transform, (4.118a) and (4.118b), in the familiar form

$$x' = x\cosh(g\tau/2c) - ct\sinh(g\tau/2c), \tag{4.119}$$
$$t' = t\cosh(g\tau/2c) - (x/c)\sinh(g\tau/2c). \tag{4.120}$$

From the second equality in (4.113) we have

$$t + x/c = K(t - x/c), \tag{4.121}$$

where

$$K = \left(\frac{1+\beta}{1-\beta}\right)^{1/2} \tag{4.122}$$

is the longitudinal Doppler shift, while from the first and third equalities, it follows that $K = e^{g\tau/c}$.

Consequently,

$$x/ct = \tanh(g\tau/2c) = \frac{\cosh(g\tau/c) - 1}{\sinh(g\tau/c)}. \tag{4.123}$$

But, this implies that the first of the transform equations, (4.119), vanishes identically, $x' = 0$, and the second relation, (4.120), reduces to

$$t' = t\ \mathrm{sech}(g\tau/2c) = t\sqrt{(1-(x/ct)^2)}. \tag{4.124}$$

Equation (4.124) can be considered as an expression of time dilatation in a frame of uniform acceleration.

To see what these imply, we consider a "momentary rest frame." This is an inertial frame whose velocity is equal to that of the particle. Viewed in this frame, the mass of the particle is its rest mass, but the particle is undergoing an acceleration g. Thus, its position, x', as well as its velocity, $\dot{x}'$, is zero in the momentary rest frame, but, its acceleration is $\ddot{x}' = g$. In contrast to the stationary frame, the acceleration is not constant, but, rather, decreases in time as:

$$a = \frac{g}{1 + (gt/c)^2}.$$

Introducing (4.123) into (4.114), and realizing that it is the double angle formula for the hyperbolic tangent, we get the rapidity,

$$\beta = \tanh(g\tau/c), \tag{4.125}$$

[1] As $\beta \to 1$, $\alpha \to \infty$, so there is no limit on the hyperbolic measure of the velocity.

showing that the velocity, $u = \mathrm{d}x/\mathrm{d}t$, still obeys the Poincaré addition law (4.114) of velocities even though we are not dealing with uniform motion.

Returning to the equation of motion of uniform acceleration in time, (4.117), we integrate it, and using (4.125) we get:

$$gt/c = \sinh(g\tau/c) = \frac{\beta}{\sqrt{(1-\beta^2)}}, \tag{4.126}$$

for $u = 0$ at $t = 0$. The fact that the hyperbolic time τ is the only additive time seems to have been overlooked in (Møller 1952). Multiplying (4.126) by (4.123) and using the second equality in the latter yield

$$xg = c^2 \left(\cosh(g\tau/c) - 1\right). \tag{4.127}$$

Finally, multiplying both sides of (4.127) by the change in mass yields the work (4.110), viz.,

$$W = \Delta mgx = Q_2 \left(\cosh(g\tau/c) - 1\right), \tag{4.128}$$

where we have identified the heat (4.109) as the heat given up to the cold reservoir.

From relation (4.126) it follows that

$$\cosh(g\tau/c) = \frac{1}{\sqrt{(1-\beta^2)}} = \sqrt{(1 + (gt/c)^2)}. \tag{4.129}$$

Thus, (4.128) allows the heat absorbed at the furnace to be written as:

$$Q_1 = \Delta mc\sqrt{(c^2 + (gt)^2)}. \tag{4.130}$$

This provides a direct relation between heat and gravity. In the limit as $g \to \infty$, (4.130) becomes $Q_1 = F \cdot ct$, where $F = \Delta mg$ is the weight. The temperature of the furnace is $T_1 = T_2\sqrt{(1 + (gt/c)^2)}$, which becomes infinite in the limit as $g \to \infty$, meaning that work without limit can be extracted from such an engine!

As τ approaches infinity, the work (4.110) also approaches infinity because T_2 approaches zero since the velocity u approaches the speed of light. Taking the time derivative of (4.110), we find the power as

$$\dot{W} = \dot{Q}_1 \left[1 - \sqrt{(1-\beta^2)}\right] + G \cdot a, \tag{4.131}$$

where

$$G = \gamma \Delta mu \tag{4.132}$$

is the momentum and a is the acceleration. The term $G \cdot a$ is the power necessary to keep the system in a state of uniform acceleration. In the limit of infinite time, the rate of working is equal to the rate of heating, $\dot{W} = \dot{Q}_1$.

Introducing the rate of change of the heat rejected at the cold reservoir, (4.109), into (4.131), and with the aid of (4.111), we come out with the important relation

$$\frac{\dot{Q}_1}{T_1} - \frac{\dot{Q}_2}{T_2} = \frac{G \cdot a}{T_2}. \tag{4.133}$$

In words, (4.133) states that *the algebraic sum of the rates of heating divided by the temperatures at which they are at is equal to the power necessary to keep the system in a state of uniformly accelerated motion, divided by the temperature of the condenser*.

For an inertial system, the acceleration vanishes, and (4.133) gives the kinetic analog of Clausius' criterion for reversibility, $\sum \dot{Q}/T = 0$. $G \cdot a$ is the minimum power consumption; for irreversible processes, $T_2 > \gamma^{-1} T_1$, and the equality in (4.133) is transformed into an inequality, viz.,

$$\frac{\dot{Q}_1}{T_1} - \frac{\dot{Q}_2}{T_2} > \frac{G \cdot a}{T_2}. \tag{4.134}$$

Inequality (4.134) says that a greater entropy production will result when additional irreversible processes are present other than the minimum power consumption, $G \cdot a/T_2$, which is necessary to keep the system in a state of uniform acceleration.

4.2.7 Coefficient of Performance from the Complementary Efficiency of a Refrigerator

The purpose of a refrigerator is to extract as much heat as possible, Q_c, from the cold reservoir. This is known as the "refrigeration" effect: a positive heat transfer from the cold reservoir. In order to be able to compare reversible and irreversible cycles, $Q_c \leq Q_c^{\text{rev}}$, both cycles must experience the same negative net work transfer, and both must experience heat transfer from the same two reservoirs. Since the heat absorbed in an irreversible cycle is less than in a reversible cycle, it is necessary that the heat transfer to the hot reservoir be smaller *in the algebraic sense* for a reversible cycle than for an irreversible cycle.

A complementary efficiency to the expression in the nonmaximal work (4.14) may be defined as

$$W^{\dagger} = -Q_h\left(\frac{T_h - T_c}{T_h}\right) \ln\left(\frac{T_h}{T_h - T_c}\right), \tag{4.135}$$

where $-Q_\mathrm{h} > 0$ is the heat transferred to the high temperature reservoir. Imposing the condition of reversibility (4.15), and using inequality (4.13), the upper bound to (4.135) is found to be

$$
\begin{aligned}
W^\dagger &= \Big(-Q_\mathrm{h} + Q_\mathrm{c}\Big)\ln\Big(\frac{T_\mathrm{h}}{T_\mathrm{h}-T_\mathrm{c}}\Big) \\
&\leq \omega(-W) = -\frac{T_\mathrm{c}}{T_\mathrm{h}}Q_\mathrm{h} = Q_\mathrm{c},
\end{aligned}
\tag{4.136}
$$

where

$$
-W = -Q_\mathrm{h} + Q_\mathrm{c} \tag{4.137}
$$

is the negative net work transfer, and

$$
\omega := \frac{T_\mathrm{c}}{T_\mathrm{h}-T_\mathrm{c}} \tag{4.138}
$$

is the coefficient of performance (COP). The COP is defined as the refrigeration effect or the positive heat transfer from the cold heat reservoir, Q_c, to the hot reservoir, $-Q_\mathrm{h}$.

Inequality (4.136) shows that the refrigeration effect is smaller for an irreversible cycle than for a reversible cycle. In order to make a comparison between the two cycles, the same negative net work transfer must be made between the same two heat reservoirs. This requires the heat transfer to the hot reservoir to be smaller *in the algebraic sense* for the reversible cycle than for the irreversible cycle, since it absorbs more heat at the cold reservoir.

4.3 Beyond Steam Engines: Thermoelectricity

After having mastered the thermodynamics of steam engines, both Thomson and Clausius turned their attention to other ways of producing work. Even in a perfectly homogeneous conductor there are intrinsic electric forces if it is not at a uniform temperature. And even when the temperature is the same throughout, there are intrinsic electric forces when the conductor is not entirely homogeneous. Strain which produces temperature differences also alters the intrinsic electric forces, and in crystalline materials the thermoelectric quantities will vary in different directions. When current passes from one material to another, or from cold to hot in a single material, there will be in addition to frictional heating, reversible thermal effects that produce heating or cooling depending on the direction of the current.

As early as 1821, Seebeck discovered that in a closed circuit comprised of two metals when their junctions are maintained at different temperatures an electric current will flow around the circuit. If the metals are copper and iron and one of the junctions is heated to a temperature not exceeding 600°C then an electric current is created across the hot junction in the direction from copper to iron. Such

thermoelectric circuits can be made to do mechanical work, and it was seen by both Thomson and Clausius as an alternative to a steam engine for generating power. But, the source of such work was not as obvious as in the heating of steam.

In 1834 Peltier gave further insight into the origin of such an energy source. He discovered that when a current flows across a junction formed from two different metals, there is an absorption, or release, of heat. If a current flows in one direction across the junction and heat absorption occurs, it will inevitably generate heat when the current is reversed. Moreover, if the current flows in the same direction as the current at the hot junction, heat will be absorbed, while, if it flows in the same direction as the current in the cold junction, heat will be given off. The heat liberated or absorbed was found to be directly proportional to the quantity of electricity which passes through the junction. The amount of heat that is absorbed, or released, when a unit charge crosses the junction is referred to as the Peltier effect at the temperature of the junction.

We now can fashion this thermal electrical effect as a Carnot engine. For suppose we place one iron–copper junction in a hot compartment and the other in a cold compartment. A current will be produced that flows from the copper to the iron in the hot compartment, while from the iron to the copper in the cold compartment. On the basis of Peltier's discovery, this thermoelectric current will absorb heat in the hot compartment and release heat in the cold compartment. The thermoelectric current therefore plays the role of the working substance in the Carnot engine, so that the thermoelectric couple can be used in place of the ordinary steam engine. Both Thomson and Clausius came to this realization, but it was Thomson who gave a greater contribution to the formulation of the theory.

Experiments carried out on thermoelectric currents can give ulterior confirmation of the view that one is dealing entirely with thermal energy. The current passing through the circuit absorbs heat at the hot junction and releases heat at the cold junction. There was no indication that other forms of energy were involved, such as chemical energy from changes in the nature of the junctions. But, could the thermoelectric circuit be treated as a reversible thermal engine?

In order for the circuit to be reversible, the same thermal processes should occur in reverse order when the circuit is reversed. It was known from the work of Fourier that heat conduction occurs along metals when there exist a difference of temperature, and from the work of Joule there is a heating effect proportional to the square of the current which is impervious to the direction of the current. If these effects could be considered as second order, we may treat the circuit as a reversible engine to first order. In order for such to be the case, Thomson argued that the Peltier effect cannot be the only reversible thermal process in the circuit.

Assume, for the moment, that the Peltier effect is the only reversible process that occurs in the circuit. Let Q_{c} stand for the mechanical quantity of heat that is released at the cold junction which is kept at temperature T_{c}. Suppose that Q_{h} is the Peltier heat absorbed at the hot junction which is maintained at temperature T_{h}. Since the circuit is reversible, we require

$$\frac{Q_{\mathrm{c}}}{T_{\mathrm{c}}} = \frac{Q_{\mathrm{h}}}{T_{\mathrm{h}}},$$

but, this must be

$$= \frac{\text{Work done when a unit charge traverses the circuit}}{T_\mathrm{h} - T_\mathrm{c}}.$$

Now, the work done when a unit of electricity travels around a closed circuit is the electromotive force $\mathcal{E}$, so that the latter is given by

$$\mathcal{E} = \frac{Q_\mathrm{c}}{T_\mathrm{c}} \left(T_\mathrm{h} - T_\mathrm{c}\right). \tag{4.139}$$

If this were true, it would mean that the hotter the hot junction, the greater the electromotive force should be. However, Cumming showed that there were circuits in which the electromotive force decreased with increasing temperature of the hot junction until a point was reached where the electromotive force is reversed causing the current to flow in the opposite direction! Thomson was forced to conclude that there were other reversible thermal effects involved related to the flow of current along an unequally heated conductor. Through a painstaking series of experiments, Thomson was able to establish the reality of such reversible phenomena.

Thomson discovered that when electricity flows along a wire whose temperature varies from point to point, heat is released when the current at that point flows in the direction of heat flow. That is, when the current is flowing from hot to cold, there will be a liberation of heat, while, if the current is flowing in the direction opposite to the heat flux, there will be an absorption of heat. This is true for copper, but, not for iron where the reverse holds. Consequently, when a current flows along an unequally heated copper wire, there is a tendency to diminish the differences in temperature, while when it flows along an iron wire it tends to accentuate those differences in temperature. This is called the Thomson effect.

4.3.1 Thomsons's Theory of the Electrical Specific Heat

Thomson found that he could conveniently express his effect by introducing what he termed "the specific heat of the electricity in the metal." If p_1 and p_2 are any two points along the metallic wire at temperatures T_1 and T_2 and if this difference is assumed small, then the specific heat c_e is defined by

$$c_\mathrm{e} \left(T_1 - T_2\right) = \mathcal{Q}, \tag{4.140}$$

where $\mathcal{Q}$ is the heat generated or absorbed in the segment $p_1 p_2$ when a unit of electricity passes from p_1 to p_2.

Another fact of experience is the following. If $\mathcal{E}_1$ is the electromotive force developed in a circuit when the cold junction is at temperature T_0 and the hot junction at T_1 and $\mathcal{E}_2$ is the electromotive force around the same circuit when the cold junction

is at T_1 and the hot junction at T_2, then the total electromotive force $\mathcal{E}_1 + \mathcal{E}_2$ is that of a circuit whose cold junction is at T_0 and hot junction at T_2. That is to say, the sum of the electromotive forces selects the extremal temperatures of the separate electromotive forces. As a consequence, the total electromotive force around a circuit whose temperatures lie between T_0 and T_1 is

$$\mathcal{E} = \int_{T_0}^{T_1} \Pi(t)\mathrm{d}t,$$

where $\Pi(t)$ is referred to as the thermoelectric power at temperature t.

Still another experimental fact concerns different circuits comprised of different metals all operating between the same extremal temperatures. If $\mathcal{E}_{M_i M_j}$ is the electromotive force for a circuit comprising of metals M_i and M_j and $\mathcal{E}_{M_j M_k}$ is the electromotive force for a circuit formed of metals M_j and M_k, then

$$\mathcal{E}_{M_i M_k} = \mathcal{E}_{M_i M_j} - \mathcal{E}_{M_j M_k},$$

independent of the specific nature of metal M_j, provided only that all circuits are operating between the same extremal temperatures.

4.3.2 Tait's Thermoelectric Diagrams

We have Tait (1884, p. 196) to thank for the following graphical representation of thermoelectric power. Tait plots the thermoelectric power, $\Pi(T)$, of a metal and some standard metal, such as lead, vs. the temperature. Characteristic plots are those shown in Fig. 4.8. For a small difference in temperature, Π is assumed positive when the current flows from lead to the metal across the hot junction.

From what has been said above, if the curves 1 and 2 are thermoelectric lines for metals M_1 and M_2, then at a temperature T_w the circuit made up of these two metals will have a thermoelectric power given by EF in the figure. If the cold junction is

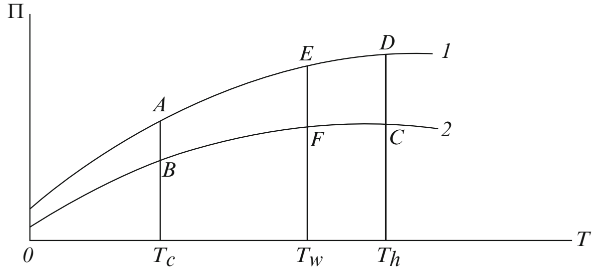


Fig. 4.8 Tait's thermoelectric diagram

at T_c and the hot junction at T_h, then the electromotive force for the whole circuit formed from metals M_1 and M_2 will be given by the area $ABCD$.

Now consider the same two metals at temperatures T_1 and T_2, where the temperature difference $(T_1 - T_2)$ is very small. Then the work done by a unit charge as it moves around the circuit, or the electromotive force of the circuit, is given by the area $ABCD$. Now let us decompose this area into the following thermal factors. First, there is the Peltier effect at the junctions. Let area A_1 stand for the mechanical equivalent of heat that is absorbed at the hot junction when a unit of electricity crosses from metal M_2 to M_1. Analogously, the area A_2 will represent the mechanical equivalent of heat released at the cold junction. Second, there is the Thomson effect due to the unequally heated metals. The mechanical equivalent of heat absorbed when a unit of electricity flows through M_2 from hot to cold junctions is represented by the area B_1. Finally, the mechanical equivalent of heat released when a unit of electricity flows through M_1 from hot to cold junctions is B_2.

According to the first law, the work is equal to the differences in heat absorbed and rejected:

$$ABCD = A_1 - A_2 + B_1 - B_2, \tag{4.141}$$

as shown in Fig. 4.9.

According to the second law, if Q is the heat absorbed in any reversible engine at temperature T, where the algebraic sign of Q accounts for whether heat is absorbed or released, then

$$\sum \frac{Q}{T} = 0.$$

If the temperatures at the two junctions differ little from one another, we may suppose that the temperature at which heat absorption takes place in the Thomson effect

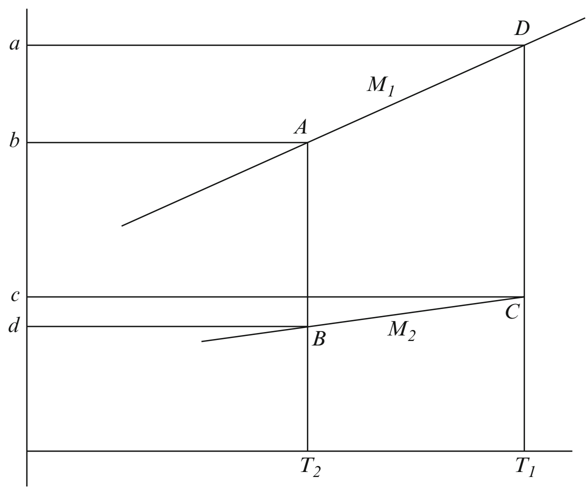


Fig. 4.9 Thermoelectric analog of a Carnot cycle

is the arithmetic mean of the two temperatures $T_A = \frac{1}{2}(T_1 + T_2)$. Thus, the second law can be stated as:

$$\frac{A_1}{T_1} - \frac{A_2}{T_2} + \frac{B_1 - B_2}{T_A} = 0. \tag{4.142}$$

Consequently, combining the first and second laws, (4.141) and (4.142), results in

$$ABCD = \frac{1}{2}\left\{\frac{A_1}{T_1} + \frac{A_2}{T_2}\right\}(T_1 - T_2)\,.$$

Now, when T_1 is near to T_2, the area

$$ABCD \simeq CD\,(T_1 - T_2)\,,$$

or $A_1 \simeq CD \cdot T_1$, which implies that A_1 is given by the area $CDac$. The indices are superfluous, and we see that the Peltier heat at any temperature is

$$\begin{aligned}\text{Peltier force} &= \Pi \cdot T \\ &= \text{(thermoelectric power)} \times \text{(absolute temperature)}.\end{aligned}$$

According to the definition of the specific heat of electricity, the difference in the Thomson heats is

$$B_1 - B_2 = (c_{e1} - c_{e2})\,T_1 T_2.$$

But, according to the first law (4.141) and $A_1 = CDac$, $A_2 = BAbd$, we find

$$\begin{aligned}B_1 - B_2 &= bADa - dBCb \\ &= (\tan\phi_1 - \tan\phi_2) \cdot T_1(T_1 - T_2),\end{aligned}$$

where ϕ_1 and ϕ_2 are angles with the tangents at A and B to the thermoelectric lines for M_1 and M_2 make with the abscissa along which the temperature is measured. Thus, it follows that

$$c_{e1} - c_{e2} = (\tan\phi_1 - \tan\phi_2)\,T_1. \tag{4.143}$$

When the temperature interval $(T_1 - T_2)$ is not infinitesimal, the areas $cCDa$ and $BAbd$ will still represent the Peltier heats at the junctions, and the area $dBCc$ will still give the absorbed heat when a unit of electricity flows along metal M_2 from the point where the temperature is T_2 to the point where it is T_1.

In the experiments carried out by Tait (1884, p. 197), he found that the specific heat of electricity was directly proportional to the absolute temperature:

$$c_e = \tan\phi \cdot T.$$

It was also known that the specific heat of electricity for lead was vanishingly small. Assume that c_e is identically zero when it refers to lead. Thus, the thermoelectric power Π for any metal with respect to lead is

$$\Pi = \tan\phi(T - T_0),$$

where T_0 is the so-called "neutral point" of the metal and lead. That is, T_0 is the absolute temperature at which the lines of the metal and lead meet.

If for any two metals, ϕ_1 and ϕ_2 are the angles that their lines make with respect to the lead line and T_1 and T_2 are their neutral temperatures, then their thermoelectric powers with respect to lead are:

$$\begin{aligned}\Pi_1 &= \tan\phi_1(T - T_1),\\ \Pi_2 &= \tan\phi_2(T - T_2).\end{aligned}$$

The thermoelectric power of the circuit that is made up of these two metals will be

$$\Pi = (\tan\phi_1 - \tan\phi_2)(T - T_0), \tag{4.144}$$

where T_0 is their neutral temperature,

$$T_0 = \frac{T_1\tan\phi_1 - T_2\tan\phi_2}{\tan\phi_1 - \tan\phi_2},$$

which is a sort of weighted average.

Then, if T_h and T_c are the temperatures of the hot and cold junctions, respectively, the electromotive force of the circuit is

$$\mathcal{E} = \int_{T_\mathrm{c}}^{T_\mathrm{h}} \Pi\,\mathrm{d}T = (\tan\phi_1 - \tan\phi_2)\left[\frac{1}{2}(T_\mathrm{h} + T_\mathrm{c}) - T_0\right](T_\mathrm{h} - T_\mathrm{c}). \tag{4.145}$$

From this expression, Tait (1884, p. 415) concludes "that the expression for the electromotive force has no other variable factors than the two; the first $[T_h - T_c]$ of which was known to Seebeck, while the second $[\tan\phi_1 - \tan\phi_2]$ was discovered experimentally by Thomson."

Moreover, Tait notes that nothing "more than the algebraic *difference* between the specific heats of electricity in the two metals" can be measured since the same constant factor, $(\tan\phi_1 - \tan\phi_2)$, appears both in the expression for the electromotive force, (4.145), and in the Peltier effect. Furthermore, (4.145) shows that the electromotive force vanishes when the arithmetic mean temperature of the junctions is equal to the neutral temperature. Finally, if one of the junction temperatures is maintained constant and the other junction temperature is varied, the electromotive force will have a maximum or minimum value when the other junction temperature is at the neutral temperature.

Although Tait followed Thomson in his exposition, we have chosen to follow (J.J.) Thomson (1921) in our treatment. Most modern treatments relegate the Peltier and Seebeck effects to the linear domain of irreversible thermodynamics (De Groot 1966). (J.J.) Thomson (1888) made even an earlier (somewhat unsuccessful) attempt to derive the properties of thermoelectricity from a classical mechanical approach involving a Lagrangian which distinguished between "controllable," as opposed to "uncontrollable," coordinates, where the former were related to work while latter obviously represented quantities related to heat. The fact of the matter is that the founders of thermodynamics were able to encorporate both the Seebeck and Peltier effects within the realm of classical thermodynamics through the employment of the Thomson effect.

4.3.3 Clausius's Thermoelectric Theory

Again a clash of ideas occurred between Clausius and Kelvin, the former claiming that the specific heat of electricity, (4.140), as far as he was aware, gave no explanation as to the cause of thermoelectric currents. According to Clausius, the electromotive forces that occur at junctions of different metals are of thermal origin. They are functions of temperature and vary in such a way that fall within the domain of the second law, i.e., reversible heating effects.

If the junctions are at the same temperature, the electromotive forces balance one another, and no current flows. Rather, if the temperatures of the junctions are different, a current is setup, with the second law demanding that the contact force vary with temperature. The complete electromotive force is

$$\mathcal{E} = \Pi\,(T_1 - T_2)\,, \tag{4.146}$$

where Π is a constant depending on the nature of the metals and T_1 and T_2 are the junction temperatures. Essentially (4.146) is Thomson's (4.139). Deviations from normal thermoelectric behavior could occur at high temperatures which, according to Clausius, altered molecular composition. Clausius cites that the thermoelectric properties of strained and unstrained wires of the same material can be completely different. But, the supposed changes in structure were considered to be reversible, for, if, heating the material and then cooling it back to the original temperature the same structure is recovered.

In place of the sum of terminal Peltier forces, $\Pi\,(T_1 - T_2)$, Clausius considers the differences $(\Pi_1 T_1 - \Pi_2 T_2)$, where Π_1 and Π_2 are the values of Π at the junction temperatures T_1 and T_2. In metals such as copper, the forces are small due to small variations in Π, so that the electromotive force between a junction at temperature T will be due to the product of T and the small variation $\mathrm{d}\Pi$ in Π, viz., $T\,\mathrm{d}\Pi$. The sum over all junctions, $\sum T_i \mathrm{d}\Pi_i$, will represent the total electromotive force.

The difference of potential, $P = \Pi T$, or the Peltier force, varies as the temperature of the copper varies. Suppose we divide the copper wire into four pieces

with Peltier forces P_1, P_2, P_3, and P_4. The terminal forces in the copper are joint to the lead, whose junctions have the potential differences, $-P$ and P_4. The intermediate forces are $P_1 - P_2$, $P_2 - P_3$, and $P_3 - P_4$. Their sum is simply $P_1 - P_4$, which cancels the junction force with lead, $P_4 - P_1$, and thereby leaves no resultant electromotive force.

This is the characteristic property of a force which is derived from a potential: the integral around a closed circuit vanishes. In fact, if we consider the increment in the Peltier force,

$$\mathrm{d}\,(\Pi T) = \Pi\,\mathrm{d}T + T\,\mathrm{d}\Pi,$$

we get two terms, the first being the resultant increase in the electromotive force and the second is the integral force in the copper wire. If we consider five separate and distinct temperatures in the wire, T_0, T_1, T_2, T_3, and T_4, we can write the sum of the first term as

$$\begin{aligned}&-T_0\Pi_1 + (\Pi_1 - \Pi_2)\,T_1\\ &+ (\Pi_2 - \Pi_3)\,T_2 + (\Pi_3 - \Pi_4)\,T_3 + \Pi_4 T_4.\end{aligned}$$

The first and last terms are the Peltier forces at the junctions with lead, while the middle terms have the form $\sum T\mathrm{d}\Pi$, which are the increments in the intrinsic forces.

Now, the terms can be arranged to read

$$\begin{aligned}&(T_1 - T_0)\,\Pi_1\\ &+ (T_2 - T_1)\,\Pi_2 + (T_3 - T_2)\,\Pi_3 + (T_4 - T_3)\,\Pi_4,\end{aligned}$$

which has the form $\sum \Pi\mathrm{d}T$, or the increment in the electromotive force. It shows that the increment in the complete electromotive force is equal to the complete integral force within the copper wire, which can only be the case if the constitutive relations between Π and T is linear and symmetric. Moreover, if we consider the force in the copper per unit length, $T(\mathrm{d}\Pi/\mathrm{d}x)$, in the direction of decreasing Π and consider similar variations in the temperature per unit length, then on the basis of Fourier's law of heat conduction we will arrive at the linear laws of irreversible thermodynamics relating nonconjugate causes (forces) to effects (flows). Although these laws impose a symmetry in the transport coefficient matrix, the symmetry is other than Onsagerian, because their origins are not to be found in the principle of microscopic reversibility (Lavenda 1978). According to this principle, the forward and backward transition rates are equal at equilibrium.

Although such relations apply to chemical reactions, they can hardly be expected to hold for a variety of thermoelectric effects which can be defined in terms of three transport coefficients, or in terms of the thermal and electrical conductivities, and the thermoelectric power.

4.4 Irreversibility Viewed as Violations in the First and Second Laws

The closest anyone has come to relating Carnot's theory to (nonconventional) thermodynamics is Lervig (1972). He associates the "loss of work" in Carnot's theory with the increase in entropy in Clausius's theory. While it is true that irreversible processes are "described by the second law, they are in Carnot's theory described by the first law." However, in Carnot's theory this requires the existence of the entropy function to show that all accessible states from a given state requires the increase in internal energy. Accessibility means that work must be done to cause a change in the state of a system and this cannot be done under adiabatic conditions.

Thomson argues that work can only be done by "letting down" heat to a lower temperature. Carnot contends that the maximum amount of work is the difference in the heat absorbed to that rejected

$$W_{\text{max}} = Q_{\text{h}} - Q_{\text{c}}. \tag{4.147}$$

He has no reason to doubt otherwise. Implicit in Carnot's statement (4.147) is the second law. So Carnot accepts the second law, but is ignorant of the first law. In general, the work will be less than that given by (4.147) due to dissipation. But, there must still be a balance of energy,

$$W = Q_{\text{h}} - Q_{\text{c}} - \Delta E, \tag{4.148}$$

where $\Delta E > 0$. That is to say, there cannot be any other sources of work other than what the engine does, for, otherwise, the heat given up to the cold reservoir would not be a limiting factor on the efficiency of the engine. According to Carnot, $\Delta E < 0$ would result in a perpetual motion of the second kind.

Combining (4.147) and (4.148) results in

$$W = W_{\text{max}} - \Delta E. \tag{4.149}$$

Therefore, in the presence of irreversibility Carnot negates the existence of a function of state called the internal energy.

Now, Clausius accepts the first law

$$W = Q_{\text{h}} - Q_{\text{c}}, \tag{4.150}$$

in all circumstances, whether they be reversible or not. However, he notes that, in general,

$$W \leq W_{\text{max}} = \eta_{\text{C}} Q_{\text{h}}, \tag{4.151}$$

so that he is negating the existence of an entropy function in the presence of irreversibility. That is to say, inserting (4.150) into (4.151) results in

$$\frac{Q_{\mathrm{h}}}{T_{\mathrm{h}}}-\frac{Q_{\mathrm{c}}}{T_{\mathrm{c}}}=-\Delta S\leq 0, \tag{4.152}$$

which is his famous inequality that bears his name. All that (4.152) says is that more heat is ceded to the cold reservoir than (4.15), in the event that the process was reversible.

Now, introducing (4.150) into (4.152) results in

$$W=Q_{\mathrm{h}}-Q_{\mathrm{c}}=W_{\max}-T_{\mathrm{c}}\Delta S. \tag{4.153}$$

Thus, Clausius negates the existence of a function of state, called by him the entropy, in the presence of irreversible processes. Comparing Carnot's negation of the first law, (4.149), with Clausius's negation of the second law, (4.153), gives

$$\Delta E=T_{\mathrm{c}}\Delta S. \tag{4.154}$$

This represents the heat rejected to the cold reservoir in excess of the smallest possible quantity, (4.15), and it depends only on the temperature of the cold reservoir, T_{c}.

Enter Thomson (1852a). We shall quote freely from Tait (1868). If $\mathrm{d}Q$ is the heat available for doing work, its *practical* value will be

$$\mathrm{d}W=\frac{T-T_{\mathrm{c}}}{T}\mathrm{d}Q, \tag{4.155}$$

where T_{c} is the lowest possible temperature. Tait then goes on to say that in any cyclical process, if Q_{h} is the heat absorbed and Q_{c} is the heat released, then the practical value is

$$W=Q_{\mathrm{h}}-Q_{\mathrm{c}}-T_{\mathrm{c}}\int\frac{\mathrm{d}Q}{T}. \tag{4.156}$$

If the cycle is reversible, the work will be the difference $(Q_{\mathrm{h}}-Q_{\mathrm{c}})$, on the strength of the first law. This demands that the integral term in (4.156) vanish. In general, however, this integral has a finite *positive* value because "in nonreversible cycles the practical value of the heat is always less than $Q_{\mathrm{h}}-Q_{\mathrm{c}}$." Hence, the amount of heat lost needlessly, i.e., other than to the refrigerator or in producing work, is

$$T_{\mathrm{c}}\int\frac{\mathrm{d}Q}{T}\geq 0. \tag{4.157}$$

This is Thomson's expression for the amount of heat *dissipated* during the cycle.

Thomson's inequality is in blatant contradiction with Clausius's (4.152). After having succeeded to confuse a great number of people, including Clerk-Maxwell himself, Tait (1884) retracts (4.157), but, without making any sense. According to Tait,

> the work will be simply the excess of the heat taken from some of the bodies over that given to others. This must always, except when perfect engines are employed, be *less* than the realizable value [(4.156)]. Hence, we see that the expression [(4.157)] is necessarily *negative*; except when perfect engines only are used, *in which case alone its value is zero*. This is Thomson's expression for the heat dissipated during the cycle of operations.

As we have quoted from Clerk-Maxwell in the Preface, he was eventually set right by Gibbs, who was influenced by Clausius, and the German school, and not by Kelvin. Corrections to his little black book can be found in later editions; in particular, the tenth edition edited by Lord Rayleigh in 1891.

Tait's reasoning contradicts the fact that there is *more* excess heat available to perform work! The point Thomson and Tait missed was this: Their "practical" value, (4.155), is the maximum work that can be realized, since the cycle is reversible. No matter how many engines that are coupled to the system, it still remains the maximum work. Since they equate the work with the difference in the net heat, Thomson and Tait are adhering to the first law, viz. there exists a function of state, the internal energy. The last term in (4.156) can only be the difference between the maximum work, that is performed in a reversible cycle, and the actual work that is done. Hence, Thomson and Tait do, in fact, obtain Clausius's inequality (4.152). Therefore, there was no reason why Tait's book should have lost the credibility it did for having reversed Clausius's inequality. Even in more contemporary, authoritative books on the history of thermodynamics (Cardwell 1971, pp. 266–267) one finds Clausius's inequality reversed!

Moreover, the heat $Q_{\mathrm{c}} \geq T_{\mathrm{c}} Q_{\mathrm{h}}/T_{\mathrm{h}}$ must be given up to the cold reservoir, since there is no other means of getting rid of it. There is nothing in Carnot's formulation that other dissipative processes exist which detract heat away from the ability to perform work. What about work that is performed in adiabatic processes? Again, there is no provision in Carnot's conception of an engine to be able to get work from nothing. This is the reason that the specific nature of the adiabatic expansion and compression is not required. All that is important is that in order to be able to perform work, heat must be "let down" from a higher to a lower temperature. In Carnot's sense, Carathéodory's formulation of the second law is completely superfluous since work must be done in order that a change in the state of the system to occur.

As we already know, as early as 1853, Thomson (1853) derives the amount of work that could be gotten when perfect thermodynamic engines are introduced into an irregularly heated body that reduce each of its parts to a single common temperature. If m_i is the mass of the ith element of an irregularly heated body, with specific heat at constant volume, $c_v(T_i)$, at temperature, T_i, then the perfect engines will operate in such a way that all the heat lost is transformed into work with the body

reaching a common temperature T_M. The condition that no heat should be given out to any other body at temperature T_M is:

$$\sum_i^n m_i \int_{T_i}^{T_M} \frac{c_{vi}(t)}{t} \mathrm{d}t = 0. \tag{4.158}$$

Thomson uses (4.158) to determine T_M. Then he employs

$$W = \sum_i^n m_i \int_{T_M}^{T_i} c_{vi}(t) \mathrm{d}t \tag{4.159}$$

to determine the maximum work done. Observe that (4.158) is the condition that thermal equilibrium is achieved under adiabatic conditions, and the work (4.159) is the negative change in the internal energy so that (4.158) and (4.159) are expressions of the second and first laws when no heat transfer takes place.

Denote by T_c the temperature of the coldest element. In this event all the heat will be converted into work, and there will be no heat that can be given off to a condenser above that in which adiabatic equilibration occurs. If the body resembles an ideal gas and the masses have a common specific heat, c_v, then the maximum work is

$$\begin{aligned} W_{\max} &= c_v \sum_{i=1}^n m_i \int_{T_f}^{T_i} \mathrm{d}t \left(1 - \frac{T_\mathrm{c}}{t}\right) \\ &= c_v \sum_{i=1}^n m_i \left\{ \sum_{i=1}^n m_i T_i \Big/ \sum_{i=1}^n m_i - T_f \right\} + T_\mathrm{c} \Delta S, \end{aligned} \tag{4.160}$$

where the change in entropy

$$\Delta S = c_v \sum_{i=1}^n m_i \ln \left(T_f \Big/ \left(\prod_{i=1}^n T_i^{m_i} \right)^{1/\sum_{i=1}^n m_i} \right). \tag{4.161}$$

If $T_f > \left(\prod_{i=1}^n T_i^{m_i} \right)^{1/\sum_{i=1}^n m_i}$, more heat will be given off to the condenser than if it were at the geometric mean temperature, thereby decreasing the work.

The minimum possible value of T_c is the geometric mean temperature, for which the entropy change (4.161) vanishes. *This final common temperature is achieved by letting the hot reservoir at T_h come into thermal contact with the cold reservoir at temperature T_c. In the Carnot cycle this is avoided by allowing the working fluid to undergo adiabatic expansion and compression which lowers and increases its temperature, respectively.* Carnot knew fully well that the hot and cold reservoirs could not be allowed to come into thermal contact for, otherwise, no work could be achieved. This is none other than the principle of maximum work.

The minimum change in energy is given by (4.154), which in this case is

$$\Delta E = c_v \sum_{i=1}^{n} m_i T_c \ln\left(\frac{T_c}{T_G}\right), \tag{4.162}$$

where $T_G = \left(\prod_{i=1}^{n} T_i^{m_i}\right)^{1/\sum_{i=1}^{n} m_i}$ is the geometric mean temperature. Due to its convex nature, (4.162) can be considered to contain information of the lowest mean temperature with respect to the geometric mean, T_G. It is positive semidefinite, i.e., $\Delta E \geq 0$ with equality if and only if $T_c = T_G$.

Since the cells are initially adiabatically isolated, we can transform (4.160) into the maximum work done by an "endoreversible" engine. The hottest cell at T_1 absorbs an amount of heat Q_1. Since we have the hierarchy,

$$T_1 > \sum_{i=1}^{n} m_i T_i \Big/ \sum_{i=1}^{n} m_i \geq T_c \geq \left(\prod_{i=1}^{n} T_i^{m_i}\right)^{1/\sum_{i=1}^{n} m_i} > T_2, \tag{4.163}$$

the maximum work is

$$W_{\max} = c_v \sum_{i=1}^{n} m_i \left\{ T_1 - T_c + T_c \ln\left(T_c \Big/ \left(\prod_{i=1}^{n} T_i^{m_i}\right)^{1/\sum_{i=1}^{n} m_i}\right)\right\}. \tag{4.164}$$

If adiabatic equilibration takes place, the last term vanishes, and for a system of two equal masses, $m_1 = m_2 = m$, (4.164) reduces to

$$W_{\max} = Q_1\left(1 - \sqrt{\left(\frac{T_2}{T_1}\right)}\right), \tag{4.165}$$

where $Q_1 = 2mc_vT_1$ and $T_c = \sqrt{(T_1T_2)}$. Expression (4.165) gives precisely the efficiency of the endoreversible engine, which is what Thomson found for an unequally heated body which was allowed to come to a uniform final temperature and equipped with perfect engines. Thomson's analysis precedes the endoreversible engine by a century and a quarter.